

MODERN PRACTICAL CHEMISTRY

BY

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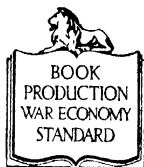
A. E. Bell



LONDON

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*Printed in Great Britain at the St Ann's Press,
Tunbridge Wells, Kent*

PREFACE

This book is designed to meet the needs of students who are studying Chemistry for such examinations as Higher School Certificate, London Intermediate, and First M.B. examinations. It is hoped that it will be found adequate for a two-year course. The book has originated in the desire to import the ideas of modern theoretical chemistry into the laboratory so far as this is possible at this stage. Considerable advances have been made during recent years, and these are clearly reflected in modern theoretical works. Unfortunately it is easier to learn the new ideas as abstractions than to see their applications, and there is always a danger of theory running ahead of practice. The author believes that it is during this introductory course as much as at the university that most students form their mental habits. It is thus of great importance that the laboratory work should be correlated to a considerable degree with theoretical studies.

This, although widely recognised, is difficult to secure in practice. No apology is therefore tendered for introducing a short discussion of certain theoretical principles into this textbook. The treatment of the whole of the practical work within the covers of one book may go some way towards achieving success in this difficult problem. It is not, of course, intended that the book should make reference to larger works unnecessary. It is assumed that larger works are kept for consultation. Nevertheless, this book is complete in itself and contains all the necessary data for the experiments described. Appropriate reference to theory, it is hoped, will secure some of that elusive "transfer" of training so that, whatever his problem, the student will come to see his experiments in relation to governing theoretical principles. It has been preoccupation with this problem that has led to the writing of this book.

It will be seen that, although it is not large enough to serve as a work of reference, this book contains much more than any student could be expected to do during a two-year course. Selection of exercises is therefore necessary. For the more experienced student some less common problems have been included. No experiments offering unusual experimental difficulty or requiring an excessive expenditure of time have been included. Although the greater part of the work has been dictated by examination requirements, some exercises have been included which have less inevitability about them. This has necessitated a good deal of investigation.

The only references given in the text are to two excellent small introductory works by Dr. J. C. Speakman: *Modern Atomic Theory* (1938) and *An Introduction to the Modern Theory of Valency* (1943). These convey the stimulating ideas of the larger works by Sidgwick and Pauling, and are at the same time of a suitable size and scope for the

beginner. The author hopes that in endeavouring to relate laboratory experience with modern ideas concerning chemical combination he has not forgotten the high traditions of technique and manipulative training which must be maintained if the student is in time to become a true chemist. It is important that the student should be encouraged to use the larger and more specialised works as he becomes proficient—works amongst which the following might in particular be instanced: Treadwell and Hall, *Analytical Chemistry*. 2 vols. 1944; A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*. 1943; Willard and Furman, *Elementary Quantitative Analysis*. 1936; L. Vanino, *Präparative Chemie*. 2 vols. 1925; A. King, *Inorganic Preparations*. 1936; J. B. Cohen, *Practical Organic Chemistry*. 1937; Mann and Saunders, *Practical Organic Chemistry*. 1940; A. Findlay, *Practical Physical Chemistry*. 1941.

Mr. L. S. Price, M.A., B.Sc., of Bradfield College, and Dr. H. Irving of St. Edmund Hall, Oxford, made some very valuable suggestions when the book was being written, and Mr. G. E. Coates, M.A., B.Sc., of Bristol University, contributed some noteworthy improvements after reading the proofs. For this help the author offers his sincere thanks; if faults remain they are attributable to him.

A. E. B.

CLIFTON, 1946.

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MODERN PRACTICAL CHEMISTRY

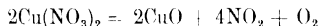
SOME THEORETICAL NOTES

These notes and others given throughout this book are included with the aim of applying theoretical knowledge at every stage of practical work. Those given in this introduction are selected on account of their wide applicability. Many of the theoretical topics discussed in this book will require a fuller treatment elsewhere : it is with the *application* of principles that we are here really concerned.

A great deal of practical work in Chemistry requires an acquaintance with the properties of the commoner elements and their simpler compounds. It must be presumed that the student has followed an introductory course and that he is familiar with the simpler sorts of reaction. A knowledge of the general methods of making oxides and salts, for example, is essential. These, very briefly, are as follows.

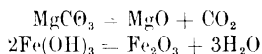
Preparation of Oxides.

1. Oxidation of an element by heating in air
2. Decomposition by heat of the nitrates of most heavy metals, e.g. :



Mercury and silver nitrates, however, too readily change to the metal on heating since the oxides are unstable at high temperatures.

3. Decomposition by heat of the carbonates and hydroxides of heavy metals, e.g. .

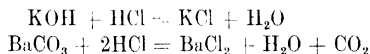


In some cases the so-called carbonates and hydroxides are really basic salts (cf. copper "carbonate" and "hydroxide").

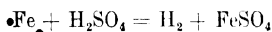
Preparation of Salts.

The common methods may be considered with reference to the position of the metal in the electrochemical series (p. 9).

1. The salts of strongly electro-positive elements (Li, K, Ba, Na) are most often made from the hydroxides or carbonates, e.g. :



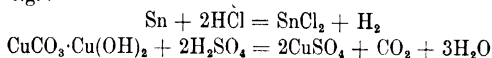
2. Rather less electro-positive elements (Mg, Al, Zn, Fe) may be treated with dilute acids, e.g. :



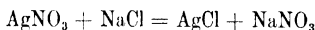
3. Metals just preceding hydrogen and immediately following (Ni, Sn, Pb, Cu, Hg), require in general the action of concentrated acid. Alter-

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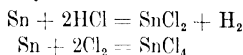
natively the oxide or carbonate (i.e. basic carbonate) may be treated with dilute acid, e.g.:



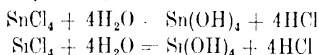
4. Sparingly soluble salts are almost invariably made by precipitation e.g.:



5. Anhydrous chlorides of heavy metals are made by the action of hydrogen chloride or chlorine. Where the element forms two chlorides the lower chloride will generally be formed by the action of hydrogen chloride and the higher by chlorine.



A simple classification of oxides as (a) basic, (b) acidic, (c) amphoteric, (d) neutral, (e) peroxides will no doubt be familiar. Metallic oxides are as a class typified by basic character, non-metallic oxides are in general typified by acidic character. Allied with this difference is the behaviour of the chlorides of the elements when mixed with water or aqueous alkali. While the chlorides of electropositive elements are stable in water, those of the less electropositive elements and the electronegative elements are, or tend to be, hydrolysed, e.g.:



Valency.

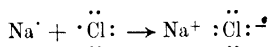
The development of the theory of the nuclear atom and the electronic theory of valency has meant the transformation of the study of Chemistry. Chemical compounds become more interesting in the light of the new knowledge, and their changes are more easily understood. Corresponding roughly to the opposite kinds of chloride mentioned above we now recognise *electrovalent* and *covalent* compounds as distinct classes. Sodium chloride, an electrolyte, ionised in solution and in the solid state, is a typical electrovalent compound. Sulphur monochloride (p. 141) is purely covalent; no chloride ions are liberated by this compound and the link between the sulphur and chlorine atoms is of a different kind from that formed when sodium and chlorine unite. An account of the mode of formation of these links is given in many modern textbooks but Speakman's *An Introduction to the Modern Theory of Valency* is especially valuable* (see Chapters I-V at this stage).

All that can be said here is that the formation of all kinds of valency link is bound up with the attainment of stable groups or "shells" of electrons for the atoms combined together. The structures of the atoms of the inert gases supply a remarkable clue to some of these stable groupings, and these groupings are the ones attained in very many of the commoner elements when they form compounds.

* Numerous references to this work are given at various points in this book.

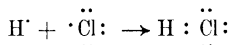
VALENCY

In the formation of an electrovalent link an electron is completely transferred from one atom (the electropositive element) to the other (the electronegative element):



Written in this way the dots represent the electrons in the valency shell only. The resulting ions are held together by electrostatic attraction, but in water the substance becomes dissociated and the solution has the properties of an electrolyte.

A covalent link is formed by the sharing of two electrons in the simplest case. One electron is contributed by each atom and an electrically neutral molecule is formed. In this way both atoms may attain a stable electron shell.



Under certain conditions a covalent link may undergo transition to the electrovalent condition. Thus, in water the chlorine atom in hydrogen chloride assumes complete control over the bond electrons, leaving a bare hydrogen nucleus or proton. This is immediately hydrated (p. 5). In benzene solution hydrogen chloride remains in the covalent state.

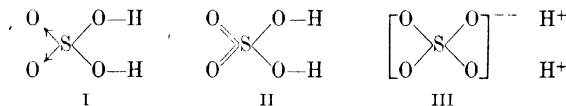
Double covalent bonds $\diagup \text{C} = \text{C} \diagdown$, and triple bonds $-\text{C} \equiv \text{C}-$ are common in certain compounds of carbon. These in general show "unsaturation". the compounds are reactive and show a tendency to add on other atoms, thus being converted to structures of single bonds only.

Physical methods such as diffraction of X-rays, measurement of dielectric constant and heat of formation, are now largely used to investigate the nature of chemical links. Not all links are found to fall into the two categories of purely covalent and electrovalent links, and modern work makes it increasingly more difficult to represent valency any longer in a purely numerical way. Methods of representing the facts may indeed have to be changed. For example, what were once thought to be double bonds in certain compounds are now represented as *co-ordinate* or *co-ionic* links. The attainment of stable electronic groupings is brought about in these cases by an atom contributing *both* of the electrons required for a covalent link. While the link, once formed, is practically indistinguishable from an ordinary covalent link it lacks the comparative symmetry associated with the latter and there is a slight difference of charge on the atoms joined. Symbols for this link are $\text{A} \rightarrow \text{B}$ or $\text{A}^+ \leftarrow \text{B}^-$.

Covalent links alone possess the property of direction in space. In this connection co-ordinate links are similar; they are to be regarded as a special type of covalent link ("dative covalency" is another name). The existence of a directive property leads, among carbon compounds in particular, to the existence of isomerism and stereoisomerism.

It remains to be mentioned that all three types of link may be involved

in one compound. Sulphuric acid, for example, is thought to be a covalent compound with the structure I or II when it is in the anhydrous state.



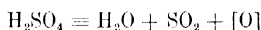
In water the ionised form III is present. In III the four oxygen bonds are shown in a non-committal way because of ignorance as to their exact nature.

It will be clear that it is only in a somewhat formal sense that one can speak of a *molecule* of an ionised compound, or consequently, of the *molecular weight* of such a compound.

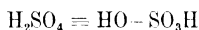
Behaviour of Reagents.

The more familiar acids and alkalis in dilute solution behave as ionic reagents and may be thought of as mere sources of hydrogen and hydroxyl ions respectively. As the solutions are made more concentrated the behaviour in some cases is not so simple. Thus, while dilute sulphuric acid provides H^+ and SO_4^{--} ions (or more correctly H_3O^+ and SO_4^{--} ions—see p. 5) the more concentrated solutions behave as if mainly H^+ and HSO_4^- ions and H_2SO_4 molecules were present. It then shows its properties as

(a) an oxidising agent

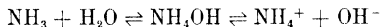


(b) a sulphonating agent (see p. 198)



Strong hydrochloric acid also behaves as if unionised molecules were present. The solution smells of hydrogen chloride, and this gas is easily expelled by the addition of concentrated sulphuric acid.

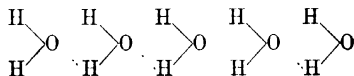
Strong ammonia solution contains relatively few hydroxyl ions and there is undoubtedly an equilibrium between the ions and the unionised hydroxide :



The dilute solution is much used as an alkali since it is easy to drive off the excess by heat. The presence of NH_3 molecules in strong ammonia solution explains its use in the preparation of amines (see p. 151).

Solution.

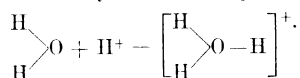
The best solvent for electrovalent (and the general class of polar) compounds is water. Water is known to be an associated liquid, that is, it is composed, not mainly of single molecules, H_2O , but of chains of these molecules :



An explanation of this process of "hydrogen bonding" can be given only by reference to the principle of "resonance." An explanation of this principle cannot be given here,* but a number of illustrations of resonance effects will be found in later pages.

The association of water, its high dielectric constant and its solvent action are no doubt related facts. It is a very poor solvent for covalent compounds as a class. These dissolve best in non-associated or "normal" liquids like benzene. Water and other associated liquids are termed abnormal solvents.

The laws of solution which we possess are applicable only for conditions of great dilution. The theory of solution given in textbooks of Physical Chemistry regards dilute solutions as analogous with gases, the solvent being a kind of "dead space" occupied by the solute molecules. While this is a fruitful conception it cannot strictly be applied to solutions of ordinary strength. We do not know very much about the extent to which molecules or ions are combined with the solvent in most cases, but there is no doubt that definite chemical union can occur. The most important case is that of the oxonium (or hydroxonium) ion H_3O^+ . This is formed by co-ordination of a hydrogen ion (or proton) by a water molecule :



Simple hydrogen ions are thought to be rare in aqueous solution. Experiment shows that in general metallic ions are hydrated and that anions come next in importance.

It should be noted that we often use the word "dissolve" for cases in which a chemical change is involved. Thus zinc "dissolves" in hydrochloric acid, silver chloride "dissolves" in ammonia solution, calcium sulphate "dissolves" in ammonium sulphate solution. The reasons for the formation of a solution in these cases vary—the last two depend on the formation of a complex ion and of a double sulphate respectively. Many "insoluble" salts can be got into solution by making use of complex ion formation, and this is a common procedure in qualitative analysis.

Strictly speaking we should never refer to any salt as insoluble since experiment shows that all known "insoluble" salts do possess some slight solubility which may be detected by electrical conductivity methods. The best method of comparing the solubilities of sparingly soluble salts is to refer to tables of the solubility products (see p. 8).

Action of Heat.

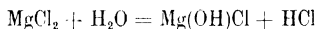
It is unfortunately not possible to give any general rules about the rupture of chemical links by the action of heat. The readiness with which a compound is decomposed in this way is closely connected with the question whether the products are themselves stable substances. Thus ammonium chloride breaks up into ammonia and hydrogen chloride quite

* Cf. Speakman, *Valency*, p. 77.

readily, but sodium chloride, which if decomposed would give sodium and chlorine atoms, can be fused and even vaporised (1441° C.) without decomposition.

Many salts are decomposed by heat into an acidic and a basic oxide, e.g. the carbonates of calcium and heavy metals. When the acidic oxide is unstable at high temperatures, as is the case with nitrogen pentoxide, a lower oxide is formed. Thus the nitrates of many heavy metals give the metal oxide, oxygen and nitrogen peroxide. The alkali metal nitrates are much more stable and when decomposed do so in a different way, yielding the nitrite and oxygen. Sulphates in general require a higher temperature for their decomposition, and for this reason are little used for the preparation of metallic oxides.

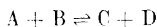
When water of crystallisation is present this is usually liberated at a low temperature. The salts of weak bases are often extensively hydrolysed, on heating, by their own water of crystallisation (see p. 15). Thus the chlorides of Cu^{++} , Mg^{++} , Zn^{++} , Al^{+++} , Sn^{++} , Bi^{+++} , Cr^{+++} , Fe^{+++} are among those which evolve a certain amount of hydrogen chloride and leave a residue of basic chloride, e.g.



Few inorganic salts will withstand high temperatures without *any* decomposition. Sodium carbonate, used for volumetric analysis, should not be heated above 300° C., but even at 1000° C. the loss of carbon dioxide from an open crucible is very slow. For purposes other than its use as an analytical reagent sodium carbonate can be regarded as stable to heat. Even calcium carbonate requires a high temperature and a current of air for the loss of carbon dioxide to be appreciably fast.

Law of Mass Action.

When a chemical reaction is reversible :



it is a well-known fact that complete conversion of the reactants into the products is not achieved *unless* one of these is removed as it is formed from the reaction mixture. Guldberg and Waage (1864) stated the law that the rate of chemical reaction is proportional to the active mass of a reactant, and this provides the basis of a simple treatment of a large number of problems. It follows from this treatment that the rate of reaction is given by

$$r_1 = k_1[\text{A}][\text{B}]$$

All quantities are measured in gram-molecules per litre. The assumption is that the active masses are equal to the gram-molecular concentrations (gram-molecules per litre) written []. k_1 is then the velocity constant for the change.

It is simple to show that when a state of equilibrium has been reached in the above reversible change

$$\frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = \frac{k_1}{k_2} = \text{constant (K)}$$

LAW OF MASS ACTION

The constant K is termed the equilibrium constant. For gas reactions the partial pressures may be used :

$$\frac{p_C p_D}{p_A p_B} = K$$

It is no longer accepted that molar concentration represents active mass, but the new treatment in terms of "activities" is not needed at this stage *provided* we realise that the molar concentrations can be used for low concentrations only.

The significance of the equilibrium constant is that it tells us the extent to which a reaction will go from left to right. Since it is independent of the amounts of reactants initially present it follows that the presence of a large excess of A will ensure the fullest conversion of B. This fact is of importance in many preparations in organic chemistry since one of the reactants may be expensive or difficult to make.

The Theory of Ionisation.

Typical electrovalent compounds, like the alkali halides, are ionised completely in the solid state and in solution. The term *dissociation* is applied to the separation of the ions in solution so that they behave independently in the carrying of current and in cryoscopic effects. It is considered that such compounds as the alkali halides provide no simple molecules, but that electrostatic forces between the ions lead to the practical immobilisation of a certain proportion of the ions at any instant. The mobility of the ions, in carrying an electric current, is reduced by a kind of electric viscosity. In solutions of weak electrolytes, which are only feebly dissociated, the same retarding forces are at work, but the effect is slight owing to the low concentration of ions.

In 1888 Ostwald showed that the dissociation of weak electrolytes like acetic acid is in accordance with the law of Mass Action.



Hence

$$\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = K$$

where K is the dissociation constant. This is now accepted as the best *criterion* of a weak electrolyte. The values of the dissociation constant vary widely. For acetic acid and ammonium hydroxide the value is 1.8×10^{-5} ; for hydrocyanic acid it is 7.2×10^{-10} . No constant is obtained in the case of salts or strong acids and alkalis. These are believed to be practically completely dissociated. Certain experimental facts were formerly supposed to indicate 90 per cent. or more in very many cases, but even this estimate is now thought to be too low.

One of the most striking results which emerges from a study of ionic dissociation is that the sodium and even the ammonium salts of weak acids like acetic acid are almost as strongly dissociated as sodium chloride. The reason for this is that the hydrogen ion can go over to the covalent state owing to its small size relative to the anion. The arguments advanced

by Fajans explain the greater difficulty attending such a change in the case of cations of large volume—such as Na^+ , K^+ .

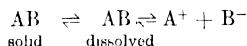
Another useful conclusion is that dibasic and tribasic acids dissociate in stages :



The second stage dissociation is always weaker than the first since it of course requires more work to remove the second H^+ ion from the negatively charged HA^- ion. It is not surprising, therefore, that when they are sufficiently stable, crystalline bisulphates separate from reaction mixtures containing concentrated sulphuric acid. The bisulphates of alkali metals are well known ; those of bivalent metals are somewhat unstable.

Solubility Product.

The application of the law of Mass Action to the ionisation of a binary electrolyte gives us, as above, the formula for the dissociation constant. If the compound is sparingly soluble the bringing together of its ions in sufficient concentration will bring about precipitation. We then have the equilibria :



If the Mass Law is obeyed we have, for the second equilibrium :

$$\frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = K$$

and if excess of the solid form AB is present the denominator may be regarded as constant and we have

$$[\text{A}^+][\text{B}^-] = \text{constant (S)}$$

This derivation of the solubility product (S) cannot be regarded as satisfactory since sparingly soluble salts are certainly highly dissociated. An alternative derivation which does not require the supposition of a molecular form is indicated on p. 88. The important fact is that the equation for the constant S is found to hold good for sparingly soluble compounds even when foreign ions are present—as they commonly are—provided these do not exceed a concentration of about 0.2N to 0.3N. (For explanation of normalities see p. 47.) As will be seen, the numerical values are very small.

AgCl	1.2×10^{-10}	HgS	4.0×10^{-53}
AgBr	3.5×10^{-13}	Bi ₂ S ₃	5.6×10^{-39}
AgI	1.0×10^{-16}	Sb ₂ S ₃	3.4×10^{-31}
PbCl ₂	2.4×10^{-4}	As ₂ S ₃	4.5×10^{-33}
PbS	4.2×10^{-28}	Fe(OH) ₂	1.6×10^{-14}
HgCl ₂	2.0×10^{-21}	Fe(OH) ₃	1.1×10^{-36}
CuS	8.5×10^{-45}	Al(OH) ₃	8.5×10^{-23}
		Cr(OH) ₃	2.9×10^{-29}

The above compounds are a selection of those which are of importance in analysis.

The theory of precipitation, the common ion effect and the ionic product of water are among the topics which are discussed in the notes to the sections on analysis (p. 13 and p. 51).

The Electrochemical Series.

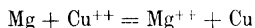
A metal in contact with a solution of its own positive ions is found to develop a difference of potential with respect to the solution. Some metals are charged positively, others negatively, under similar conditions. In the case of those which are charged negatively there can be little doubt that the magnitude of the potential difference is a rough indication of the tendency of the metal to go into solution in the form of ions. These potential differences are calculated on the arbitrary basis that hydrogen, in contact with a Molar solution of its ions, develops zero potential. In contact with Molar solutions of their own ions the more common metals give the following potentials

Li/Li ⁺	- 2.96 volts	Zn/Zn ⁺⁺	- 0.76
K/K ⁺	- 2.92	Fe/Fe ⁺⁺	- 0.44
Ba/Ba ⁺⁺	- 2.90	Cd/Cd ⁺⁺	- 0.40
Na/Na ⁺	- 2.71	Co/Co ⁺⁺	- 0.29
Mg/Mg ⁺⁺	- 2.38	Ni/Ni ⁺⁺	- 0.23
Al/Al ⁺⁺⁺	- 1.69	Sn/Sn ⁺⁺	- 0.14
Mn/Mn ⁺⁺	- 1.10	Pb/Pb ⁺⁺	- 0.12
		H ₂ /H ⁺	0.00

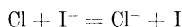
The metals which follow after hydrogen give positive electrode potentials, as also do certain non-metals. The determination of the electrode potentials of the latter is more difficult and the results are more uncertain

Cu/Cu ⁺⁺	+ 0.34	I/I	+ 0.54
Hg/Hg ⁺⁺	+ 0.85	O ₂ /OH ⁻	+ 0.40
Ag/Ag ⁺	+ 0.80	Br/Br	+ 1.10
Au/Au ⁺⁺	+ 1.36	Cl/Cl ⁻	+ 1.36

The existence of these potentials may be attributed to a tendency of the element to form an ion either by surrendering an electron or by gaining one, but quantitatively the potential is not of great value and the correlation of the table with chemical properties can be carried out only in a very general way. The more electropositive elements will displace less electropositive elements from the ionised condition:



and similarly, at the other end of the table:

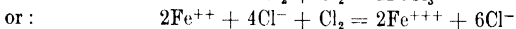
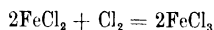


The order of the metals agrees also with their reactions with steam and with dilute acids. It appears likely that the action of an oxyacid on a metal which comes after hydrogen in the table takes place by direct action of the metal, which, by losing electrons is oxidised (see below). The theory, for example, that the reaction of concentrated sulphuric or

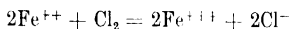
nitric acids on copper involves the intermediate formation of nascent hydrogen appears improbable.

Oxidation and Reduction.

A general conception of oxidation must embrace all cases of combination of an element with electronegative elements: oxygen, sulphur, chlorine, etc. More generally still, oxidation may be defined as an increase in the electronegative part of an electrovalent compound; the essential process being the removal of electrons from the substance oxidised. Thus we may represent the oxidation of ferrous chloride to ferric chloride as follows:



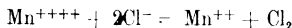
This may be reduced further by cancelling out what is common to both sides:



In the oxidation of hydrochloric acid by manganese dioxide:

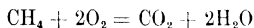


it is easy to see that the essential process is



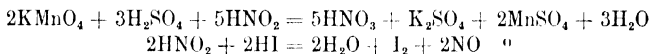
but it is necessary to assume that substances like metallic oxides can be given an ionic formula. While this is true in many cases it is not true universally.

The definition of oxidation as the removal of electrons is accordingly limited to the reactions of electrovalent compounds. In the oxidation of covalent compounds there may be no transfer of electrons, e.g.:

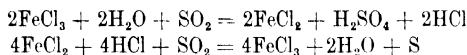


In such a case it will be found that each element has the same number of electrons in its outer shell before and after the change.

Substances must be regarded as oxidising or reducing agents in the appropriate conditions only. Nitrous acid, for example, will decolorise potassium permanganate solution, but it will also liberate iodine from acidified potassium iodide solution.

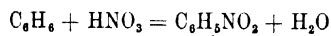


Sulphur dioxide will reduce ferric salts to ferrous salts, but it can also oxidise a concentrated solution of ferrous chloride in the presence of hydrochloric acid:



The factors of concentration and temperature often have a great influence on the course of a reaction, a fact which is well illustrated by the reactions of nitric acid on metals. A range of reduction products, from ammonia

and hydroxylamine to nitrogen peroxide may be obtained according to conditions. In organic chemistry the oxidising action of nitric acid is exhibited most commonly in dilute solution, the concentrated acid being rather a nitrating agent. When used for nitration it is therefore important to prevent dilution by the water eliminated.



QUALITATIVE ANALYSIS

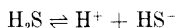
THEORETICAL PRINCIPLES

Some reference to the theory of ionic dissociation has been made in the introductory pages. Here we assume that mineral acids, the caustic alkalis and all salts are dissociated more or less completely into their ions. We have to deal with an equilibrium between ionised and unionised forms only in the case of weak acids (e.g. H_2S , CH_3COOH) and ammonia (NH_4OH).

Solubility Product and the Theory of Precipitation.

Although the orthodox elementary theory is not particularly successful in more than a qualitative way, the general principles employed in the following treatment are of considerable value. They are illustrated here chiefly by a discussion of the use of hydrogen sulphide.

Hydrogen sulphide is a very weak dibasic acid. The first stage dissociation



has a dissociation constant of 9.1×10^{-8} . For the second stage



the constant is 1.2×10^{-15} . The saturated aqueous solution at 25° contains approximately 0.1 gram-molecules per litre (0.1 molar), so it is possible to calculate the concentration of sulphide ion in gram-ions per litre.

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 9.1 \times 10^{-8}$$

and

$$[\text{H}_2\text{S}] = 0.1 \text{ and } [\text{H}^+] = [\text{HS}^-]$$

$$[\text{HS}^-]^2 = 9.1 \times 10^{-8} \times 0.1 = 9.1 \times 10^{-9}$$

$$[\text{HS}^-] = 9.5 \times 10^{-5}$$

Now

$$\frac{[\text{H}^+][\text{S}^{--}]}{[\text{HS}^-]} = 1.2 \times 10^{-15}$$

$$[\text{S}^{--}] = \frac{(1.2 \times 10^{-15})(9.5 \times 10^{-5})}{9.5 \times 10^{-5}}$$

$$= 1.2 \times 10^{-15} \text{ (gm.-ions per litre).}$$

When hydrogen sulphide is bubbled into a solution of copper sulphate in water a black precipitate of copper sulphide is formed. From the table of solubility products on p. 8 we see that

$$[\text{Cu}^{++}][\text{S}^{--}] = 8.5 \times 10^{-45}$$

* A gram-ion is the weight of the ion (from atomic weight tables) expressed in grams.

and since

$$[S^{--}] = 1.2 \times 10^{-15}$$

$$[Cu^{++}] = \frac{8.5 \times 10^{-45}}{1.2 \times 10^{-15}} = 7.1 \times 10^{-30}$$

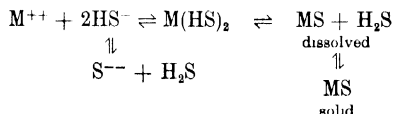
This means that there must be this concentration of copper ions present in the solution at the end. If the original solution was decinormal the change in concentration, in gram-ions per litre, as a result of precipitating the sulphide, is from 10^{-1} to 7.1×10^{-30} . In practice hydrogen sulphide is used in either acid or alkaline solution and this has a substantial effect on the result, as will be shown later.

Note on Sulphide Ion Concentration.

Many authors have questioned if sulphides are precipitated by the sulphide ion as a physical fact, and even if the process is an ionic one at all. If there are 1.2×10^{-15} gm.-ions of the ion in one litre we can, by means of the Avogadro number, calculate the number of ions in a given sample, say 10 c.c. Since the Avogadro number $N = 6.06 \times 10^{23}$ there will be, in 10 c.c. of saturated hydrogen sulphide

$$\frac{(6.06 \times 10^{23})(1.2 \times 10^{-15})}{100} = 7.27 \times 10^6 \text{ ions.}$$

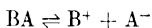
The presence of dilute acid greatly reduces this number, however, and in 0.2 N. hydrochloric acid solution, when $[S^{--}] = 3.5 \times 10^{-22}$ the number of ions in 10 c.c. would be only 2! Since sulphides can be precipitated in such concentrations of acid it appears very probable that it is the HS^- ion which is directly responsible. The process should therefore be represented by a scheme such as:



It can be shown that this would not alter the treatment of the problem from the standpoint of the law of Mass Action, i.e. sulphides are still precipitated when their solubility products are exceeded.

Common Ion Effect.

In the equilibrium of any weak electrolyte with its ions:



an increase of $[B^+]$ must mean that $[A^-]$ is decreased and $[BA]$ increased so that the expression

$$\frac{[B^+][A^-]}{[BA]} \text{ remains constant.}$$

The correctness of this idea has been tested and it appears to be satisfactory even in the case of silver chloride, which although sparingly soluble, is not a weak electrolyte. Where we can regard $[BA]$ as constant, e.g. when excess solid is present in contact with the solution, we obtain

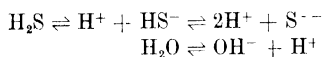
the usual formula for the solubility product: $[B^+][A^-] = \text{constant}$. It follows that by increasing $[B^+]$ we can reduce $[A^-]$ as far as we please—and vice versa (provided that no secondary changes such as complex ion formation occur). The presence of a large concentration of hydrogen ion must therefore cause the reduction of the sulphide ion concentration in solutions of hydrogen sulphide. In 0.2 N hydrochloric acid, as mentioned, the concentration of sulphide ion in a solution saturated with the gas at 25° is calculated to be only 3.5×10^{-22} . Since a metallic sulphide is precipitated only when its solubility product is reached, there may not be enough sulphide ion present for any precipitate to be formed. The sulphides of nickel, cobalt, manganese and zinc are all of them precipitated only by a relatively high concentration of sulphide ion and they are accordingly not precipitated from such acid solutions. In this way hydrogen sulphide may be used first in acid conditions and then in alkaline to separate two groups of metallic sulphides (groups II and IV of the qualitative analysis tables).

Other common ion effects are well known and much used in effecting analytical separations. The dissociation of NH_4OH



can be "repressed" (i.e. diminished) considerably by the addition of an ammonium salt to the solution. Since ammonium salts are completely dissociated the NH_4^+ ion concentration may be so high and the OH^- ion so low that the solubility products of some metallic hydroxides cannot be reached. This is very probably the reason why NH_4OH in the presence of NH_4Cl will not precipitate the hydroxides of Ni, Co, Mn, Zn and Mg although it will precipitate those of Al, Fe and Cr. It should be noted, in passing, that the solubility products show ferric hydroxide to be much less soluble than the ferrous compound. The removal of iron by precipitation of the ferrous hydroxide is therefore unsatisfactory.

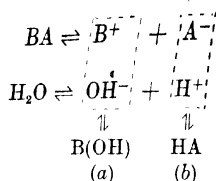
Instead of repressing the dissociation of weak acids or alkalis by the addition of common ions it is possible to increase the dissociation in certain cases. If hydrogen sulphide is absorbed in a feebly alkaline solution of a nickel salt the sulphide is precipitated, whereas in acid solution no precipitate is formed. Here we have to consider the equilibria:



Since water is practically unionised the presence of a large concentration of OH^- ions causes the withdrawal of H^+ ions to form H_2O . The removal of H^+ ions causes more H_2S to dissociate so as to maintain the dissociation constant. In this way the S^{--} ion concentration is greatly increased.

Hydrolysis.

The fact that practically all salts are highly dissociated, whereas the corresponding acids or bases may be feebly dissociated, leads to the phenomenon of hydrolysis. In the scheme



either of the equilibria (a) or (b) may be present; or both equilibria may exist. This depends on whether the base $B(OH)$ or the acid HA is strong or weak or whether both are weak—as in ammonium acetate. Sodium acetate solution behaves as an alkali because acetic acid is a weak acid; the removal of H^+ ions to form unionised acetic acid means that to restore equilibrium more water must dissociate. There is consequently an excess of OH^- ions present. If the base is weak instead of the acid, a hydroxide (or a basic salt) may be precipitated. Bismuth chloride, dissolved in excess hydrochloric acid, gives a white precipitate of the oxychloride on dilution with water.

Turbidity of solution is frequently caused by hydrolysis, and if this is due to the separation of a hydroxide or basic salt all that is necessary is to reduce drastically the concentration of OH^- ion so that the solubility product cannot be attained. This is done quite simply by the addition of some mineral acid. Provided there is no "double decomposition" any strong (i.e. strongly dissociated) acid will do.

Notes on Manipulation.

The first rule of analysis is *cleanliness*. Test tubes should be cleaned and filled with water when put away in the rack. The apparatus cupboard or drawer should be checked so as to see that it contains the ordinary apparatus and there is no accumulation of other things. During work the bench should be kept clear of unnecessary bottles and, above all, clean and dry.

In trying to obtain a solution of a solid use only very small quantities during preliminary tests so as to obviate filtration as far as possible. Do not heat test tubes which are much more than half full, and when heating, heat evenly and with gentle shaking or stirring.

Shaking a test tube with the thumb on the open end is obviously inadvisable when it contains strong acid or alkali. It is also not safe (a) when gases are evolved, and (b) when the test tube contains a hot solution. In the latter case the expansion of the air may cause unexpected spurting.

If the evolution of an inflammable gas is slow and it is desired to apply a light, it is a good plan to place a small piece of paper over the open end for a minute or two so as to reduce dilution with the air.

Much time may be saved by decanting a solution prior to filtering off a precipitate. Use as narrow a beaker as possible; leave the ppt. to settle and then gently incline the beaker so as to pour off the supernatant liquid as far as possible.

When filtering off a solid the filter paper should never project above the edge of the funnel. The paper should be folded in pleats for filtering a hot solution or whenever the ppt. is not required afterwards. When a ppt. is to be removed from the paper the ordinary method of folding in quarters should be used. If the ppt. is bulky the simplest method of removal is to take the paper out of the funnel, open it out carefully, and then to lay it face downwards over an evaporating basin. On tapping gently with the fingers the ppt. disengages itself. Alternatively the ppt. may be scraped off the open filter paper with a spatula.

If the ppt. is to be dissolved in a reagent the paper need not be removed from the funnel. With the end of a glass rod a hole is made in the filter paper and the ppt. is then washed through with a little water from the wash bottle, or using a little of the reagent (provided this is not concentrated sulphuric or nitric acid which attack filter paper).

Reagents Employed in Qualitative Analysis

The following are the reagents which are most frequently required, together with the formulae by which (for brevity) they are represented on occasions in the text.

Dilute and concentrated hydrochloric acid	HCl
Dilute and concentrated sulphuric acid	H ₂ SO ₄
Dilute and concentrated nitric acid	HNO ₃
Dilute acetic acid	HAc
Dilute sodium hydroxide (caustic soda)	NaOH
Dilute ammonium hydroxide	NH ₄ OH
Ammonium chloride solution	NH ₄ Cl
Ammonium chloride solid	NH ₄ Cl
Ammonium carbonate solution	(NH ₄) ₂ CO ₃
Ammonium sulphide solution	(NH ₄) ₂ S _x
Calcium sulphate solution	CaSO ₄
Sodium phosphate solution	Na ₂ HPO ₄
Barium nitrate solution	Ba(NO ₃) ₂
Barium chloride solution	BaCl ₂
Silver nitrate solution	AgNO ₃

Bench reagents, when dilute, are usually about 3N or 5N (N = Normal, cf. p. 47).

Also required are :

Strong ammonia solution (density 0.88 gm./c.c.)	
Mercuric chloride solution	HgCl ₂
Stannous chloride solution	SnCl ₂
Ferric chloride solution	FeCl ₃
Ferrous sulphate crystals	FeSO ₄ ·7H ₂ O
Lead acetate solution	PbAc ₂
Ammonium molybdate solution	(NH ₄) ₂ MoO ₄
Borax	Na ₂ B ₄ O ₇ ·10H ₂ O
Cobalt nitrate solution	Co(NO ₃) ₂
Potassium dihydrogen antimonate solution	KH ₂ SbO ₄
Sodium cobaltinitrite solution	Na ₃ Co(NO ₂) ₆
Potassium dichromate solution	K ₂ Cr ₂ O ₇
Potassium ferrocyanide solution	K ₄ Fe(CN) ₆

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Potassium permanganate solution	KMnO_4
Hydrogen peroxide (10 volume or 20 volume)	H_2O_2
Manganese dioxide	MnO_2
Oxalic acid	HOx
Ammonium oxalate	NH_4Ox
Ammonium acetate	NH_4Ac
Red lead	Pb_3O_4
Sodium bismuthate	NaBiO_3
Copper turnings	
Alcohol	

Useful organic reagents :

Dimethyl glyoxime (in alcohol)
 Resorcinol (in alcohol)
 α -nitroso- β -naphthol (in water + drops of NaOH)
 Benzidine (in 10 per cent. acetic acid)

Gases :

Hydrogen sulphide—from Kipp's apparatus.
 Sulphur dioxide—from bottle of liquid sulphur dioxide.

INTRODUCTION TO THE TESTS USED IN QUALITATIVE ANALYSIS

For the student who is beginning work in this subject a good method of obtaining a grasp of the tests used is to work through a number of exercises using *known* salts. This brings a sense of familiarity with the various metallic and acid radicals—and their individual peculiarities—which will fully repay the time spent. After trying out the reactions of some representative metallic and acid radicals so as to employ each reagent at least once the student will better grasp the scheme as a whole. It is not, of course, suggested that each metal and acid radical should be examined as this would take too long.

METALLIC RADICALS

Experiments on Group I. Use solutions of the nitrates of Ag, Pb, Hg(ous).

Test.	Ag^+	Pb^{++}	Hg_2^{++}
Add dilute HCl . Boil ppt. with water. To ppt. add NH_4OH .	White ppt. Insoluble. Dissolves.	White ppt. Soluble. Insoluble.	White ppt. Insoluble. Blackens.
Add K_2CrO_4 solution. To ppt. add dilute HAc . and warm.	Dark red ppt Soluble.	Yellow ppt. Insoluble.	Brick red ppt. Soluble.

Experiments on Group II. Use solutions of the chlorides made by dissolving the salts in water or the oxides in dilute HCl. Acidify the solution slightly with HCl.

Test	Hg ⁺⁺	Bi ⁺⁺⁺	Cu ⁺⁺	Cd ⁺⁺
Pass H ₂ S through solution. To ppt. add NaOH + few drops (NH ₄) ₂ S _x . See if ppt. dissolves in hot dilute HNO ₃ .	Black ppt. Insoluble. Insoluble (goes white.*)	Black to brown ppt Insoluble. Soluble.	Black ppt. Insoluble. Soluble.	Yellow ppt. Insoluble. Soluble.
To solution add NH ₄ OH in excess.	White ppt. Insoluble in excess.†	White ppt. Insoluble in excess.	Light blue ppt. soluble in excess to dark blue solution.	White ppt. Soluble in excess.

The remaining four metals of this group differ in that their sulphides are soluble in yellow ammonium sulphide solution. The above are designated Group IIA and the following Group IIB.

Test.	As ⁺⁺⁺	Sn ⁺⁺	Sn ⁺⁺⁺⁺	Sb ⁺⁺⁺
Pass H ₂ S through solution. To ppt. add NaOH + a few drops (NH ₄) ₂ S _x . See if ppt. dissolves in hot dilute HNO ₃ .	Yellow ppt. Soluble. Soluble.	Brown ppt. Soluble. Soluble.	Yellow ppt. Soluble. Soluble.	Orange ppt. Soluble. Soluble.
To solution add NH ₄ OH in excess.	No ppt.	White ppt. Insoluble in excess.	White ppt. Insoluble in excess.	White ppt. Insoluble in excess.

* The sulphide is converted into the white Hg(NO₃)₂·2HgS.

† "Infusible white precipitate" HgNH₂Cl.

Experiments on Group III. Use solutions of the sulphates or chlorides.

Test	Fe ⁺⁺⁺	Al ⁺⁺⁺	Cr ⁺⁺⁺
Add a little NH_4Cl solution and then NH_4OH . To ppt. add NaOH in excess. If solution formed add H_2O_2 and warm.	Red-brown ppt. Ppt. insoluble. —	White ppt. Ppt. soluble. —	Dull green ppt. Ppt. soluble. Yellow solution.

Experiments on Group IV. Use solutions of the sulphates.

Test.	Co ⁺⁺	Ni ⁺⁺	Mn ⁺⁺	Zn ⁺⁺
Add a little NH_4Cl solution and then NH_4OH . Then pass H_2S .	Colour change from pink to brown. Black ppt.	Colour change from green to blue. Black ppt.	Slight brown ppt. may form. Flesh-colored ppt. turns brown on filter.	No change. White ppt.
Borax bead test on ppt. if black (p. 25).	Deep blue.	Reddish brown.		

Experiments on Group V. Use solutions of the chlorides or nitrates.

Test.	Ca ⁺⁺	Sr ⁺⁺	Ba ⁺⁺
To solution add NH_4Cl , NH_4OH and then $(\text{NH}_4)_2\text{CO}_3$ solution. Wash ppt. on filter and do flame test (p. 30).	White ppt. Brick red.	White ppt. Crimson.	White ppt. Green.
To solution add CaSO_4 solution.	No ppt.	Faint ppt. on standing.	Immediate heavy ppt.

Experiments on Group VI. There is no group reagent. Use magnesium sulphate or nitrate solution, potassium and sodium chloride solutions.

1. To a solution containing Mg^{++} add $(NH_4)_2CO_3$ solution: white ppt. Then add NH_4Cl solution: the ppt. will redissolve when sufficient NH_4Cl has been added.*

To a solution containing Mg^{++} add a little solid NH_4Cl , NH_4OH and then Na_2HPO_4 solution in excess: a white crystalline ppt. is formed. Its formation may be hastened by scratching the side of the test-tube with a glass rod.

2.† To a solution containing K^+ add a freshly prepared solution of sodium cobaltinitrite (in acetic acid): yellow crystalline ppt.

Test the solution containing K^+ with litmus paper. If acid, add a little solid sodium acetate; if alkaline, neutralise with acetic acid. Add excess sodium hydrogen tartrate solution or saturated tartaric acid and scratch with a glass rod: white ppt.

Flame test: Lilac. Visible through cobalt blue glass (see p. 30).

3. To a solution containing Na^+ add a few drops of NH_4OH to make slightly alkaline, heat to boiling and add a boiling solution of potassium dihydrogen antimonate (potassium "pyroantimonate"): white granular ppt.

Flame test: Persistent yellow (see p. 30).

* This is not a case of there now being insufficient CO_3^{--} ions, in the presence of Cl^- ions the complex ion $[MgCl_3]^-$ is formed and there are then fewer Mg^{++} ions in solution.

† Ammonium salts also give these tests.

ACID RADICALS

Introductory tests on the Reactions of Common Acid Radicals :
Use sodium or potassium salts for the following experiments.

Two general reactions are much used :

Test A : Add dilute HCl to the solid salt. If no reaction takes place in the cold, or if the reaction is slow, the mixture is warmed.

Test B : A little concentrated sulphuric acid is added very cautiously to the solid salt. In testing a simple salt this test need not be carried out if a positive reaction is obtained in *A*. It must be remembered that if dilute HCl produces effervescence, a much more violent effervescence must be expected with concentrated H_2SO_4 .

Acid radical.	Test A.	Confirmatory test.
Carbonate, bicarbonate.	CO_2 given off. Gas turns lime water milky.	—
Nitrite.	Red-brown fumes of N_2O_4 acid to moist litmus paper	Solution of nitrite + FeSO_4 solution and acidified with HAc: dark brown colour.
Hypochlorite.	Chlorine given off: reddens and then bleaches litmus.	A drop of cobalt nitrate solution added to hypochlorite solution gives a black ppt.
Sulphite.	SO_2 evolved (smell). Gas turns dichromate paper green.	Sulphite solution decolorises permanganate solution.
Thiosulphate.	Same as for sulphite, but S also liberated.	Same as for sulphite.
Sulphide (FeS can be used here).	H_2S evolved (smell) Gas blackens PbAc paper.	

Acid radical.	Test B.	Confirmatory test
Chloride.	HCl gas evolved (dense fumes with NH_3).	AgNO_3 solution and a little HNO_3 added to chloride solution gives dense white ppt. soluble in NH_4OH .
Bromide.	Reddish acid fumes of Br_2 + HBr. Fumes darken if MnO_2 added to mixture.	AgNO_3 test as above gives pale yellow ppt. Slightly soluble in NH_4OH .
Iodide.	Violet vapour + acid fumes (SO_2 , H_2S may be present).	AgNO_3 test as above gives pale yellow to yellow ppt. insoluble in NH_4OH .

Acid radical.	Test B.	Confirmatory test.
Fluoride.	Pungent acid gas which fumes in moist air. Mixture requires warming.	AgNO ₃ test as above gives no ppt. Warm mixture of solid fluoride + sand + drop conc. H ₂ SO ₄ : drop of water on rod becomes covered with "skin" on exposure to gas evolved.
Nitrate.	Acid fumes of HNO ₃ (+ N ₂ O ₄) on warming. Addition of copper turnings causes evolution of N ₂ O ₄ in quantity.	Place a crystal of FeSO ₄ ·7H ₂ O in a few drops of nitrate solution on a white tile and add two drops conc. H ₂ SO ₄ : brown coloration.
Formate.	Brisk evolution of CO on warming. Gas lights with blue flame.	Neutral AgNO ₃ solution + neutral solution of formate gives white ppt. going black.
Acetate.	Strong smell of acetic acid (vinegar) on warming.	Ferric chloride solution gives red coloration with neutral acetate solution. Red ppt. forms on warming.
Oxalate.	CO and CO ₂ (gas burns with difficulty and turns lime water milky). No charring takes place.	Oxalate solution + dilute H ₂ SO ₄ decolorises permanganate solution on warming.
Tartrate.	CO and CO ₂ as for oxalate but solid chars rapidly.	AgNO ₃ added to neutral tartrate solution gives white ppt. If this almost dissolved up in NH ₄ OH, mixture on warming deposits silver mirror.
Chromate, dichromate.	On warming O ₂ evolved. Relights glowing splint (reaction is slight).	Acid solution + H ₂ O ₂ gives intense blue coloration. Excess H ₂ O ₂ causes decomposition to green solution.
Chlorate.	Violent reaction (use 2 or 3 drops acid only), explosive ClO ₂ liberated.	
Sulphate, bisulphate.	No reaction.	Addition of dilute HNO ₃ and Ba(NO ₃) ₂ solution to solution of sulphate gives dense white ppt.
Phosphate.	No visible reaction.	Freshly made solution of ammonium molybdate in HNO ₃ added in excess to phosphate solution + HNO ₃ gives on warming a yellow ppt.
Arsenate.	No visible reaction.	Ammonium molybdate test as above gives yellow ppt. on boiling.
Borate.	No visible reaction.	Mix powdered solid with a little methyl alcohol in a porcelain dish. Add 5 or 10 c.c. conc. H ₂ SO ₄ and ignite vapour. Green-edged flame.

ANALYSIS OF A SIMPLE SALT

The reactions used in the introductory exercises are here employed to construct a scheme of analysis for identifying the metallic and acid radical of a simple salt. As will be seen the same group tests are employed in the analysis of a mixture of salts (p. 35), but there, of course, filtration is frequently necessary. In examining a simple salt no filtrations are necessary for the application of the group tests; a fresh sample of the substance should be employed for each group until a precipitate is obtained.

It will be evident from the foregoing exercises that the groups into which metallic radicals are divided are:

- I Sparingly soluble chlorides.
- II Sulphides which are precipitated in moderately acid conditions.
- III Hydroxides which are precipitated by a low concentration of hydroxyl ion.
- IV Sulphides which are precipitated by a high concentration of sulphide ion (alkaline conditions).
- V Sparingly soluble carbonates.
- VI Magnesium, sodium and potassium.

The test for ammonium salts should always be carried out beforehand—together with one or two other preliminary tests (below). These tests should not occupy more than a few minutes and may yield valuable information. (In recording the results of tests negative results should not be omitted.)

PRELIMINARY TESTS*

Record the appearance of the substance, *viz.* colour and crystalline or non-crystalline appearance. If white, the salts of Cu, Fe, Mn, Cr, Co, Ni are *very probably* absent. Also absent are chromates, dichromates, oxides of Pb, Cu, Hg, Cr, Fe and all common sulphides except ZnS.

1. Action of heat on the solid. A little of the solid should be heated in a clean dry ignition tube. If a gas is evolved it may be necessary to repeat the test, using a dry test tube fitted with a right-angle delivery tube in order to test for the identity of the gas. (See table on page 25.)

2. Charcoal block reduction.⁵ A little of the substance is mixed with twice its bulk of anhydrous sodium carbonate or of fusion mixture and placed in a small hole in a charcoal block. It is then heated in the reducing flame of the blowpipe (*viz.* the air hole of the burner is closed and the tip of the blowpipe is placed in the unburnt gas in the middle of the flame).

Bead readily formed: Ag, Pb, Sn.

Incrustation (a) white: Sb, Zn, Al.

(b) yellow: Pb, Bi.

* The numbers in small print refer to explanatory notes on pp. 43-45.

Observation.	Inference.
Charring.	Tartrates (inflammable gases; smell of burnt sugar).
Darkens to black.	Citrates (CO , CO_2 acrid smell), salts of Cu, Ni, Co.
Sublimate. ¹ CO_2 (lime water).	Certain compounds of NH_4^+ , Hg and As. Carbonates of heavy metals, bicarbonates of Na, K.
$\text{CO}_2 + \text{CO}^2$ (gas burns with difficulty).	Oxalates of certain metals.
SO_3^3 (faint white pungent fumes).	Sulphates of heavy metals.
HCl gas ⁴ (pungent fumes. Dense white fumes with NH_3).	Certain chlorides (through hydrolysis).
O_2 (relights a glowing splint).	Nitrates of Na, K. Peroxides. Chlorates. Permanganates.
$\text{O}_2 + \text{N}_2\text{O}_4$ (dense brown fumes and relights a glowing splint).	Nitrates and nitrites of heavy metals.
H_2 (lights with a pop).	Certain formates on gentle heating.

A *white* incrustation should be moistened with cobalt nitrate solution and then reheated: the incrustation becomes---

(a) green: Zn.

(b) blue: Al, phosphate, borate, arsenate.

(c) pink: Mg (unreliable).

3. Test for ammonium salt. Warm a little of the solid with some caustic soda solution: evolution of ammonia indicates NH_4^+ salt (gas recognised by smell, alkaline action on litmus, dense white fumes with HCl gas). This test must not be omitted.

4. Borax bead tests.⁶ It is worth while doing this test only if the solid is coloured. It can be used as a confirmatory test after a group test.

Some powdered borax is melted on a small loop of platinum wire (or the end of an asbestos stick). A *trace* of the solid is then taken up on the hot bead and caused to dissolve by heating to redness in the outer part of the flame.

Colour when hot.	Colour when cold.	Metal
Green.	Blue.	Cu
Brown or red.	Yellow.	Fe
Emerald green.	Emerald green.	Cr
Deep blue.	Deep blue.	Co
	Reddish brown.	Ni

METALLIC RADICALS. (Simple Salt)

In making a solution use about 2 gm. of the solid and try the following solvents in this order :

Water.

Dilute HCl.

Concentrated HCl.

Dilute HNO_3 .

Concentrated HNO_3 .

Aqua regia (3 vols. conc. HCl + 1 vol. conc. HNO_3).

If the substance will not dissolve in any of these reagents it must be examined by the preliminary tests and also by the action of concentrated sulphuric acid (see note 6 on p. 34).

Group I. These metals need be tested for only if the solution has been made up in water or in nitric acid. If HCl was used to obtain a solution these metals must be absent.

Add a little dilute HCl to the cold solution. If a ppt. is formed it will be PbCl_2 , AgCl or Hg_2Cl_2 .

PbCl_2 soluble in hot water. Hot solution + K_2CrO_4 solution gives a yellow ppt. of PbCrO_4 which is insoluble in acetic acid.

Hg_2Cl_2 blackened by the addition of a little warm NH_4OH .

AgCl dissolves in NH_4OH (an excess must be added).

Group II. The solution must not contain a large excess of acid. If concentrated acid was used to obtain a solution it must now be considerably diluted.

Warm the solution to about 60° and treat with H_2S . If no ppt. is formed dilute to 4 or 5 times the original volume and pass more H_2S . If a ppt. is formed it will be

Group IIA : HgS , Bi_2S_3 , CuS , CdS

Group IIB As_2S_3 , SnS , SnS_2 , Sb_2S_3 *

(A milky ppt. (of sulphur) which does not settle indicates the presence of an oxidising agent, e.g. nitrate, chromate. This will in most cases not prevent the identification of a true ppt. if one is also formed. Alternative procedure is given on p. 36.)

	Colour.	Action of (NH ₄) ₂ S _x .	Action of hot dilute HNO ₃ .	Original solution + excess NH ₄ OH.
HgS	Black.	Insoluble.	Insoluble (goes white)	White ppt. insoluble in excess.
Bi ₂ S ₃ *	Black to brown.	Insoluble.	Soluble.	White ppt. insoluble in excess
CuS	Black.	Insoluble.	Soluble.	Light blue ppt. soluble in excess to dark blue solution.
CdS	Yellow.	Insoluble.	Soluble.	White ppt. soluble in excess.
As ₂ S ₃	Yellow.	Soluble.	Soluble.	No ppt.
SnS	Brown.	Soluble.	Soluble.	White ppt. insoluble in excess.
SnS ₂	Yellow.	Soluble.	Soluble.	White ppt. insoluble in excess.
Sb ₂ S ₃	Orange.	Soluble.	Soluble.	White ppt. insoluble in excess.

Confirmatory tests.

- Hg⁺⁺ Add SnCl₂ solution to the original solution. A white ppt. turning grey then black is formed.⁸
- Bi⁺⁺⁺ Pour original solution (in HCl) into much water. milkiness develops. Solution does not clear on addition of tartaric acid.⁹
- Cu⁺⁺ The formation of the dark blue solution in NH₄OH is a specific test.
- Cd⁺⁺ The insolubility of the sulphide in (NH₄)₂S_x is sufficient to distinguish CdS from As₂S₃.
- As⁺⁺⁺ Flettman's Test: original solid + Al turnings + KOH solution on warming gives *extremely poisonous* arsine AsH₃. A filter paper moistened with AgNO₃ held in the mouth of the tube develops a black stain.
- Sn⁺⁺ Original solution + HgCl₂ solution gives a white ppt. turning grey, then black.⁸
- Sn⁺⁺⁺ The action of NH₄OH on the original solution distinguishes from As⁺⁺⁺.
- Sb⁺⁺⁺ Pour original solution (in HCl) into much water. milkiness develops. Solution clears on addition of tartaric acid.¹⁰

Group III.* The solution must first be tested for the presence of a ferrous salt. A few drops of potassium ferricyanide solution are added to a little of the original acid solution. If a dark blue ppt. is obtained the solution must be oxidised before proceeding to Group III. A few drops of concentrated HNO_3 are added and the mixture is warmed. The ordinary group reagent (below) can now be used.

To the solution add 1-2 gm. of solid NH_4Cl , heat to boiling and add a slight excess of NH_4OH . The solution is then alkaline and smells of ammonia. If a ppt. is formed it will be $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$.¹¹

	Colour.	Action of NaOH on ppt	Confirmatory test.
$\text{Fe}(\text{OH})_3$	Red- brown	Insoluble.	Original solution warmed with HNO_3 and then $\text{K}_4\text{Fe}(\text{CN})_6$ added: dark blue ppt.
$\text{Cr}(\text{OH})_3$	Green.	Soluble.	Boil ppt. with NaOH and H_2O_2 : yellow solution which gives yellow ppt. with lead acetate.
$\text{Al}(\text{OH})_3$	White.	Soluble.	To original solution add litmus and then excess NH_4OH : blue "lake."

* It is assumed that at this stage the student will not be required to identify metallic radicals in the presence of organic acids, phosphate or arsenate. The modified procedure for these is given in the tables for the treatment of mixtures, pp. 39, 40.

Group IV. To solution add 1-2 gm. of solid NH_4Cl , warm to dissolve and then add a slight excess of NH_4OH and pass H_2S . If a ppt. is formed it will be CoS , NiS , MnS or ZnS .

	Colour.	Confirmatory test.
CoS	Black.	Carry out borax bead test on the original solid. Deep blue indicates Co^{++} .
NiS	Black.	Carry out borax bead test on the original solid. Reddish-brown indicates Ni^{++} .
MnS	Grey-pink	Ppt. turns gradually brown on the filter paper. Dissolve a little of the original solid in 50 per cent. HNO_3 and boil with about 1 gm. of red lead in evaporating dish. Supernatant liquid will be pink or violet. (For use of sodium bismuthate see p. 44.)
ZnS	White.	Dissolve a little of the original solid (or the ppt.) in concentrated HNO_3 , add a little cobalt nitrate solution, soak a filter paper in the solution and then ignite the paper in a crucible: green ash. ¹²

Group V. To solution add 1-2 gm. of solid NH_4Cl , warm to dissolve and then add NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ solution. On standing a white ppt. may be formed. This may be assisted by scratching the side of the test tube with a glass rod. The ppt. will be the carbonate of Ca , Sr or Ba . All these are white.

Distinguishing tests.

(a) To a second quantity of the original solution add an equal volume of saturated CaSO_4 solution.¹³

No ppt. on standing indicates: Ca^{++}

Faint ppt. on standing: Sr^{++}

Immediate ppt.: Ba^{++}

(b) Dip a clean platinum wire in concentrated HCl and then in the original solid and carry out a flame test:

Brick red flame: Ca^{++}

Crimson flame: Sr^{++}

Green flame: Ba^{++}

Group VI. Separate tests are applied for Mg^{++} , K^+ and Na^+ . Using separate portions of the solution carry out the following:

(a) Test for Mg^{++} : Add NH_4Cl and then NH_4OH followed by excess sodium phosphate (Na_2HPO_4) solution. If Mg^{++} is present a white crystalline ppt. will be formed slowly.¹⁴ This may be hastened by scratching the side of the test tube with a glass rod.

(b) Provided Mg^{++} is absent (NH_4^+ also), test for K^+ : To the original solution add some freshly prepared sodium cobaltinitrite solution containing a little acetic acid.* If K^+ is present a yellow crystalline ppt. forms.¹⁵

(c) Test for Na^+ : Make the original solution slightly alkaline with NH_4OH and add a little potassium dihydrogen antimonate solution† ("potassium pyroantimonate"). If Na^+ is present a white ppt. is formed on scratching with a glass rod.¹⁶

Flame tests for Na and K. It must be remembered that sodium salts are very common impurities in other salts and consequently the persistent yellow flame of sodium is not proof that a given salt is a sodium salt. It is essential to show that other metals are absent. To carry out the flame test for potassium proceed as usual but examine the flame through a piece of cobalt blue glass. This acts as a filter against the yellow light of the sodium flame. Most specimens of potassium salts contain traces of sodium salt.

Flame tests are invariably carried out using a little of the solid moistened with concentrated HCl . The wire must first be cleaned by dipping in concentrated HCl and heating to incandescence. This is repeated until the wire by itself produces no coloration.

Sodium salts. Persistent yellow

Potassium salts. Lilac (somewhat transient).

* This solution is made by dissolving 1 gm. of the salt in 10 c.c. of water and filtering if necessary. Alternatively mix solutions of sodium nitrite, cobalt nitrate and a slight excess of acetic acid. Warm until all oxides of nitrogen have been evolved.

† This reagent is prepared by adding 2 gm. of potassium antimonate, K_2SbO_4 to 100 c.c. of boiling water, boiling for 5 minutes and then, when cool, adding 2 c.c. of 10 per cent KOH solution. The mixture should be left overnight before filtering. The reagent has the formula KH_2SbO_4 .

ACID RADICALS. (Simple Salt or Mixture)

These tests are identical whether the substance to be analysed is a simple salt or a mixture. It is a matter of opinion whether tests for acid radicals should be performed before or after tests for metallic radicals. The more experienced chemist will probably prefer to identify the acids while carrying out one or two preliminary tests, since certain acid radicals make necessary a modification of the ordinary procedure for metallic radicals.

The first two tests given here are useful preliminary tests and are not specific tests for particular radicals. Specific tests immediately follow.

1. *Action of dilute HCl.* Add a little dilute HCl to the solid in a test tube. Any gas that comes off in the cold should be identified before warming the mixture if possible. If no action takes place in the cold the mixture should be warmed. The smell of hydrogen chloride must then be expected. When analysing mixtures more than one reaction may occur, nevertheless two gases may be noticed to be evolved if care is taken.

Observation	Inference
CO (lime water test).	Carbonate or bicarbonate.
N ₂ O ₄ (acid red-brown fumes).	Nitrite.
Cl ₂ (yellow-green suffocating gas. Red-dens then bleaches moist blue litmus paper)	Hypochlorite or Oxidising agent.
SO ₂ (smell. Acid gas, turns dichromate green).	Sulphite.
SO ₂ + S.	Thiosulphate.
H ₂ S (smell. Blackens lead acetate paper or solution).	Sulphide.*
H ₂ (lights noisily. Pale blue flame, but yellow in contact with glass).	Free metals (Zn, Fe, Mg, Mn, Al). These will be noticed here if present.

2. *Action of concentrated H₂SO₄.* If a vigorous reaction was produced in (1) above it is advisable to start by adding a few drops of *dilute* sulphuric acid and waiting until the action ceases before adding 3 or 4 c.c. of the concentrated acid. If there was little or no reaction in (1) concentrated sulphuric acid is added *drop by drop* to a little of the solid in a clean test tube. The mixture is warmed gently if there is no action in the cold.

* Certain sulphides are not dissolved by dilute HCl and require the concentrated acid. These should be detected when trying to find a solvent for the substance.

Note. Do not dispose of *hot* concentrated sulphuric acid. Allow it to cool and then pour into a large beaker of cold water. Empty this down the sink.

Observation.	Inference.	Confirmatory test.
HCl gas (dense fumes with NH_3).	Chloride.	Add a little MnO_2 and warm. Cl_2 evolved—bleaches litmus.
$\text{HBr} + \text{Br}_2$ (red-brown acid fumes).	Bromide.	Add a little MnO_2 and warm. Br_2 evolved—dense red-brown fumes.
$\text{HI} + \text{I}_2$, also SO_2 and H_2S ? (violet vapour and acid gas).	Iodide.	
HF (pungent acid gas. Requires warming).	Fluoride.	Mix solid with sand and add conc. H_2SO_4 . Warm: SiF_4 gives a "skin" on drop of water on glass rod.
SO_2 (smell. Acid gas. Turns dichromate green).	Sulphite. Reducing agent.	
HNO_3 , also N_2O_4 ? (acid fumes. Requires warming).	Nitrate.	Add some copper turnings and warm. Brown fumes of N_2O_4 evolved.
CO (brisk evolution on warming, gas burns with blue flame).	Formate. ¹⁷	
$\text{CO} + \text{CO}_2$ (gas burns with difficulty).	Oxalate. ¹⁷ If accompanied by charring: Tartrate or Citrate.	
Acetic acid (smell of vinegar).	Acetate.	Mix solid with a little alcohol and add conc. H_2SO_4 . Warm for 1 minute, and pour into a little water. Fruity smell of ester.
A little O_2 .	Chromate, Dichromate.	
$\text{ClO}_2 + \text{Cl}_2$ (yellow-green gas. Spluttering noise. Explosion on warming (care!)).	Chlorate.	
CrO_2Cl_2 (reddish-brown fumes + red oil).	Chromate + 18 chloride together.	

Other confirmatory tests.

Oxalate : To a warm solution of the substance in dilute H_2SO_4 add drops of potassium permanganate solution. Permanganate decolorised (other reducing agent present will interfere).

Chromate or Dichromate. To solution of the substance in dilute acid add a little H_2O_2 : intense blue coloration.¹⁹

3. The next group of specific tests requires a solution of the substance in dilute HNO_3 . Any solid which does not dissolve after warming for a few minutes is filtered off and examined afterwards (6 below). Read Note 7, p. 34.

The solution is divided into four parts which are treated as follows :

(a) Silver nitrate solution is added.

White ppt. soluble immediately in NH_4OH . Chloride.²⁰

Pale yellow ppt. slightly soluble in NH_4OH . Bromide.²⁰

Pale yellow to yellow ppt. insoluble in NH_4OH . Iodide.²⁰

(b) The solution is neutralised with NH_4OH and then neutral silver nitrate solution is added :

White ppt. going black. Formate.

White ppt. When almost dissolved up in a little

NH_4OH deposits silver mirror on warming. Tartrate.

(c) A large excess of freshly made ammonium molybdate solution, strongly acidified with concentrated HNO_3 is added and the mixture gently warmed.

Yellow crystalline ppt. (hastened by scratching with glass rod).

Phosphate.²¹

Yellow ppt. on boiling.

Arsenate.

(d) Barium nitrate solution is added :

White ppt.

Sulphate.

4. *Test for nitrate.* Nitrate should have been indicated if present in (2) above. The reaction with concentrated H_2SO_4 is sometimes masked by another reaction due to a second acid radical. The following test may be performed in either of two ways :

(i) To a solution in water or dilute HCl an equal volume of cold freshly prepared ferrous sulphate solution is added. No more than about half a test tube full of the mixture is now required. About 5 c.c. of concentrated H_2SO_4 is then poured down the side of the test tube so that it runs mainly to the bottom and forms a second layer. A brown ring at the junction of the layers indicates nitrate.

(ii) Alternatively : Pour two or three drops of the solution on to a clean white tile. Place a crystal of ferrous sulphate in the solution and carefully drop one or two drops of concentrated H_2SO_4 on to the crystal. A brown coloration on the tile indicates nitrate. This method is preferred if the solution of the salt gives a ppt. with ferrous sulphate solution.

5. *Test for borate.* A little of the powdered solid is mixed with about 5 c.c. of methyl alcohol in a small porcelain basin and about 1 c.c. of concentrated H_2SO_4 is added. On lighting the alcohol vapour the flame appears green-edged if borate is present. (Note that Ba^{++} and Cu^{++} give the same result. In this case the metals must be pptd. with Na_2CO_3 solution and the ppt. filtered off.)

6. Residue insoluble in dilute HNO_3 . This should be filtered off and washed with water on the filter. If white it may contain :

Sulphates of Ba, Sr, Pb.

Chlorides of Ag, Pb, Hg(ous).

If dark coloured the solid is probably an oxide (e.g. Fe_2O_3 , Fe_3O_4 , Cr_2O_3) which dissolves very slowly in hot dilute acids (HCl being usually the best). Al_2O_3 is white, and as sometimes obtained is difficult to dissolve in acids.

Insoluble chlorides may be recognised by the action of concentrated H_2SO_4 . Recognition of an insoluble sulphate is more difficult. Fusion on the charcoal block with Na_2CO_3 leads to the formation of :

BaSO_4 or SrSO_4 : These give the corresponding sulphides. Residue on watch glass dissolves in a few drops of dilute HCl. Tests for cations may then be carried out.

PbSO_4 : Bead of lead and yellow incrustation.

7. *Identification of acid radicals after precipitation of heavy metals.* Some authorities prefer not to perform tests 3 and 4 on the salts of heavy metals. To convert to the sodium salts a little of the finely powdered solid is boiled for 5 minutes with an excess of strong Na_2CO_3 solution. The mixture is then filtered.

(3) Above is performed after acidifying part of the filtrate with HNO_3 , but in 3(d) BaCl_2 solution may be used in place of $\text{Ba}(\text{NO}_3)_2$.

(4) Above is performed after acidifying the remainder of the filtrate with HCl.

8. *Examination of a solution for acid radicals.* Tests (3) and (4) may be performed. For the remainder it will be necessary to evaporate the solution to dryness.

METALLIC RADICALS IN A MIXTURE OF SALTS

Separation of Metallic Radicals into Groups.

To show the group separation employed as clearly as possible the following table is included. The practical details are omitted, since they are given on the following pages.

Reagent: Dilute HCl. If ppt. filter.					
Group I <i>ppt.</i>	<i>Filtrate.</i> Reagent: H ₂ S in acid solution. Filter when pptn. is complete.				
Hg ⁺	Group II <i>ppt.</i>	<i>Filtrate.</i> Reagent: NH ₄ Cl + NH ₄ OH. If ppt. filter.			
Ag ⁺					
Pb ⁺⁺					
	Group III <i>ppt.</i>	<i>Filtrate.</i> Reagent: NH ₄ Cl, NH ₄ OH, H ₂ S. If ppt. filter.			
	Hg ⁺⁺				
	(Pb ⁺⁺)				
	Bi ⁺⁺⁺				
	Fe ⁺⁺⁺	Group IV <i>ppt.</i>	<i>Filtrate.</i> Reagent: NH ₄ Cl, NH ₄ OH, (NH ₄) ₂ CO ₃ . If ppt. filter.		
	Cu ⁺⁺				
	Cd ⁺⁺	Co ⁺⁺			
	Al ⁺⁺⁺				
	As ⁺⁺⁺	(PO ₄ ⁻⁻⁻)	Ni ⁺⁺	Group V <i>ppt.</i>	<i>Filtrate.</i> Examine by tests for
	Sn ⁺⁺		Mn ⁺⁺		
	Sn ⁺⁺⁺		Zn ⁺⁺	Ca ⁺⁺	Mg ⁺⁺
	Sb ⁺⁺⁺			Sr ⁺⁺	K ⁺
				Ba ⁺⁺	Na ⁺

The following are important precautions which must be taken in the performance of group tests.

1. Ensure complete precipitation in each group by carefully testing a little of the filtrate for any unprecipitated cation.

2. Wash precipitates on the filter paper with hot distilled water before examining them.

3. Make sure that no group reagent is carried forward into a group where it is not wanted. It is, for example, essential to boil off all H_2S before doing Group III. Neglect of this will mean that Group IV cations will be precipitated along with those of Group III.

4. Do not allow the solution to become too dilute through successive additions of group reagents. It is a good plan to test for the presence of each group with a little of the main solution and not to add the reagent for that group if those cations are absent. Also, solutions which become too dilute should be concentrated by gentle evaporation.

Group I. The sparingly soluble chlorides.

Reagent : Add a few drops of dilute HCl to the cold solution. If a ppt. is formed continue adding dilute HCl.

Ppt. may contain PbCl_2 , AgCl and Hg_2Cl_2 . Filter. Wash ppt. thoroughly with cold water and discard washings. Make a hole in the bottom of the filter and wash ppt. through into a beaker. Boil with water and filter hot.

<i>Residue :</i> Wash well with hot water. Pour warm NH_4OH through the filter paper.	<i>Filtrate :</i> If Pb is present crystals may separate on cooling. Add K_2CrO_4 yellow ppt. insoluble in dilute HAc indicates Pb.
<i>Residue :</i> If black Hg_2^{++} is present. ⁷	<i>Filtrate :</i> Acidify with dilute HNO_3 . White ppt. indicates Ag^+ present.

Group II. Sulphides precipitated in acid conditions.

Reagent : Warm a sample of the filtrate from Group I to about 60° and pass H_2S . If no ppt. is produced the sample is diluted considerably and more H_2S is passed. (This trial will indicate whether the main solution should be treated similarly.)

The formation of a milky ppt. of sulphur which does not settle is an indication of the presence of an oxidising agent. In many cases this does not interfere with the identification of a precipitated sulphide. If, however, difficulty is experienced a preliminary reduction of the oxidising agent may be carried out.

Preliminary reduction : SO_2 is passed through the filtrate from Group I until the solution smells of the gas. Fe^{+++} , CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ are reduced with a change in colour. Excess SO_2 is then boiled off before passing H_2S .

Ppt. may contain HgS (PbS)*, Bi_2S_3 , CuS , CdS (Group IIA)
 As_2S_3 , SnS , SnS_2 , Sb_2S_3 (Group IIB)

The ppt. should be examined before doing anything else, since it is liable to become oxidised.

* Owing to its not being completely removed in Group I.

Separation into IIA and IIB: After washing the ppt. on the filter with a little hot water it is transferred to an evaporating basin. 10 or 15 c.c. of ammonium sulphide ²⁷ solution is added and the mixture warmed for a few minutes with constant stirring. The mixture is then filtered.

Filtrate: May contain ammonium thioarsenate, thiostannate or thioantimonate.

Residue: May contain any of the sulphides belonging to Group IIA.

• These are insoluble in $(\text{NH}_4)_2\text{S}_x$.

IIA. Transfer the residue to a beaker, add 10 or 15 c.c. dilute HNO_3 and boil for 2 or 3 minutes. Filter.

<p><i>Residue:</i> If black is HgS. Dissolve in a little aqua regia dilute, and add SnCl_2 solution: white ppt. going grey confirms Hg^{+2}.</p>	<p><i>Filtrate:</i> May contain nitrates of Pb, Bi, Cu and Cd. If Pb found in Group I add a little dilute H_2SO_4 and alcohol to remove it as PbSO_4. Allow solution to stand a few minutes and then filter.</p>	<p><i>Residue:</i> Wash with water and dissolve up in NH_4Ac, add K_2CrO_4 solution: yellow ppt. of PbCrO_4 (insoluble in HAc).</p>	
<p><i>Note.</i> A brownish-yellow compound of mercuric nitrate and sulphide is sometimes obtained in place of the black sulphide.</p>	<p><i>Residue:</i> White $\text{Bi}(\text{OH})_3$. Dissolve in dilute HCl and pour into cold water: white turbidity ⁹ which is not cleared by addition of tartaric acid.*</p>	<p><i>Filtrate:</i></p>	<p>(i) If blue contains cuprammonium sulphate: Cu present. (ii) If colourless Cu absent: (i) Filtrate blue: add KCN solution drop by drop until colour discharged and then add a few drops excess. Pass H_2S: yellow ppt. indicates Cd present also.³⁰ (ii) Filtrate colourless: pass H_2S. Yellow ppt. indicates Cd only.</p>

* Alternatively: Confirm Bi with dimethylglyoxime. To solution in dilute HCl add dimethylglyoxime solution and then enough NH_4OH to make solution alkaline. Pale yellow ppt. confirms Bi.

IIB. Make the filtrate from the ammonium sulphide treatment just acid by adding concentrated HCl drop by drop (litmus paper) and warm gently. A white or nearly white ppt. indicates sulphur only
 -- IIB metals absent. If there is a coloured ppt. add 5 to 10 c.c. concentrated HCl and boil for 3 minutes.²⁸ Dilute with 5 c.c. water and filter.

<i>Residue</i> : Yellow As_2S_5 Wash with hot water. Transfer to test-tube and warm with $(NH_4)_2CO_3$ solution for 2 minutes. The sulphide is soluble.	<i>Filtrate</i> : May contain $SbCl_3$ and $SnCl_4$. Dilute with a little water and divide into three equal parts. (i) Reduce any Sn^{+++} by warming with iron filings for 3 minutes. Filter and add $HgCl_2$ solution : white ppt. going grey confirms Sn. (ii) If Sn present make solution just alkaline with NH_4OH , add about 5 gm. solid oxalic acid and about 50 c.c. water. Boil until all is dissolved and pass H_2S . Orange ppt. indicates Sb. ³¹ (iii) Sn absent : dilute to 50 c.c. and pass H_2S . Orange ppt. indicates Sb. Pour a little of the original solution in HCl into water : white turbidity which clears on addition of tartaric acid
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When it is certain that all Group II cations have been removed (further dilution of sample and H_2S passed) the filtrate which has been reserved is boiled until there is no further smell of H_2S .

Group III. Hydroxides precipitated in moderately alkaline conditions.¹¹

It is important to know if the following are present in the solution before proceeding with the group separation.

- Fe^{++} (note that Fe^{+++} is reduced in doing Group II).
- Organic acids.¹¹
- Phosphate.¹¹
- The test for Fe^{++} is potassium ferrieyanide solution which is added to a sample of the filtrate. Fe^{++} gives a dark blue colour. Ignore other colours. If Fe^{+++} is present warm the solution with about 2 c.c. concentrated HNO_3 .
- If preliminary tests indicate the presence of organic acid the solution must now be evaporated to dryness in the fume chamber, moistened with a little concentrated HNO_3 and gently ignited. The residue is then taken up in a dilute HCl and filtered if necessary.
- If phosphate is present (ammonium molybdate test, p. 33) the modified procedure given on p. 40 must be followed.

Phosphate absent : To the filtrate from Group II add 1-2 gm. of solid NH_4Cl , heat to boiling and then add a slight excess of NH_4OH . The solution is then alkaline and smells of ammonia. Filter.

The ppt. may contain $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$. Wash the ppt. with hot water and then transfer to an evaporating dish and add about 10 c.c. NaOH and 5 c.c. hydrogen peroxide. Boil until no more O_2 is evolved. Filter.

Residue	Brown $\text{Fe}(\text{OH})_3$ *	Filtrate	May contain Na_2CrO_4 and NaAlO_2 . If yellow CrO_4^{--} is present. Divide into two parts.
Dissolve in dilute HCl and add $\text{K}_4\text{Fe}(\text{CN})_6$. Blue ppt. indicates Fe^{+++} . Test original solution with		(1) Add litmus and then dilute HCl until acid. Then add NH_4OH in excess and shake. ²³ On standing a blue lake of $\text{Al}(\text{OH})_3$ and litmus indicates Al^{+++} .	(2) If solution is colourless omit. If yellow add excess HAc and then PbAc . Yellow ppt. of PbCrO_4 indicates Cr
(a) $\text{K}_4\text{Fe}(\text{CN})_6$ blue ppt. indicates Fe^{+++} ;			
(b) $\text{K}_3\text{Fe}(\text{CN})_6$ blue ppt. indicates Fe^{++} .			

* If Bi^{+++} was found in Group II it may be found to be still present in a small quantity. A little $\text{Bi}(\text{OH})_3$ (white) may therefore be obtained here. This may be ignored. It does not interfere with the tests for Fe .

Phosphate present : If phosphate is present it must be precipitated as ferric phosphate by adding excess ferric chloride solution. The excess

of this reagent is then removed by precipitation of basic ferric acetate. The presence of iron should be tested for beforehand ; if Fe^{++} is present it must be oxidised to Fe^{+++} with a little concentrated HNO_3 as mentioned above.

Treatment: The filtrate from Group II is nearly neutralised with NH_4OH ; there should not be enough to cause the precipitation of phosphates. Add about 5 c.c. of saturated ammonium acetate solution (or 2 gm. of the solid), warm slightly and then add *neutral* FeCl_3 solution drop by drop until the red colour of ferric acetate becomes permanent. The precipitate at this stage is ferric phosphate. Boil the mixture vigorously for two minutes and filter. The filtrate should be free from both phosphate and iron (the remaining iron being precipitated during boiling as basic ferric acetate and hydroxide). The filtrate is reserved for Group IV.

The precipitate may contain FePO_4 and basic acetate

AlPO_4 and basic acetate

CrPO_4 and basic acetate.

Since the colour of the iron phosphate obscures other substances present test for Cr and Al as follows . Transfer the ppt. to an evaporating basin, add about 10 c.c. water and add 1-2 gm. of sodium peroxide in small portions (care). Boil for about five minutes and dilute before filtering. Divide filtrate into two parts.

- (a) Add about 1 gm. of solid NH_4Cl and boil until only a faint smell of ammonia persists : a white flocculent ppt. indicates Al .
- (b) (Solution yellow) acidify with HAc and add lead acetate solution yellow ppt. of PbCrO_4 indicates Cr.

Group IV. Sulphides precipitated in alkaline conditions.

Reagent: Add about 2 c.c. more NH_4OH to the filtrate from **Group III** and pass H_2S for about one minute. Boil and filter. Wash the ppt. with hot water and reject washings.

Ppt. may contain CoS , NiS , MnS , and ZnS (also a little finely divided sulphur). Transfer the ppt. to an evaporating basin, add about 20 c.c. of very dilute HCl , stir well and allow to stand for five minutes (bench acid + five times its volume of water is suitable).

<p><i>Residue:</i> May contain NiS and CoS. Test with borax bead: blue: Co. brown: Ni, but if both present Ni is obscured. Dissolve ppt. in aqua regia, dilute with water and neutralise with NH_4OH. Divide into two parts:</p> <p>(a) Add dimethyl-glyoxime: Ni^{++} gives red ppt.;²⁴</p> <p>(b) Add α-nitroso-β-naphthol: Co^{++} gives brown colour.²⁵</p>	<p><i>Filtrate:</i> May contain Zn^{++} and Mn^{++}. Boil in evaporating basin to expel H_2S, then add excess NaOH. Filter.</p> <table border="1" data-bbox="347 673 797 963"> <tr> <td data-bbox="347 673 564 963"> <p><i>Residue:</i> Grey-pink $\text{Mn}(\text{OH})_2$ turns brown on filter. Boil ppt. in evap. basin with conc. HNO_3 + 1 gm. red lead. Supernatant liquid is pink or violet if Mn^{++} present * (See note 24, p. 44, for use of sodium bis-muthate.)</p> </td><td data-bbox="564 673 797 963"> <p><i>Filtrate:</i> May contain "sodium zincate." Pass H_2S: white ppt. (may be discoloured). Dissolve ppt. in a little conc. HNO_3. Add a little cobalt nitrate solution, soak a filter paper in the mixture and ignite in crucible: green ash indicates Zn †</p> </td></tr> </table>	<p><i>Residue:</i> Grey-pink $\text{Mn}(\text{OH})_2$ turns brown on filter. Boil ppt. in evap. basin with conc. HNO_3 + 1 gm. red lead. Supernatant liquid is pink or violet if Mn^{++} present * (See note 24, p. 44, for use of sodium bis-muthate.)</p>	<p><i>Filtrate:</i> May contain "sodium zincate." Pass H_2S: white ppt. (may be discoloured). Dissolve ppt. in a little conc. HNO_3. Add a little cobalt nitrate solution, soak a filter paper in the mixture and ignite in crucible: green ash indicates Zn †</p>
<p><i>Residue:</i> Grey-pink $\text{Mn}(\text{OH})_2$ turns brown on filter. Boil ppt. in evap. basin with conc. HNO_3 + 1 gm. red lead. Supernatant liquid is pink or violet if Mn^{++} present * (See note 24, p. 44, for use of sodium bis-muthate.)</p>	<p><i>Filtrate:</i> May contain "sodium zincate." Pass H_2S: white ppt. (may be discoloured). Dissolve ppt. in a little conc. HNO_3. Add a little cobalt nitrate solution, soak a filter paper in the mixture and ignite in crucible: green ash indicates Zn †</p>		

* Alternatively: Place a drop of benzidine on a filter paper, add 1 drop of NaOH and then 1 drop of HCl + Mn salt: blue oxidation product of benzidine formed if Mn^{++} present.

† Alternatively: Add a few drops of 0.88 ammonia solution to 2 c.c. of a 10 per cent. solution of resorcinol in alcohol and then a few drops of the zinc nitrate solution. A little turbidity may be noticed. On warming the test tube in hot water for five minutes a green coloration deepening to blue will be observed.

Group V. Sparingly soluble carbonates.

It is usually advisable to reduce the volume of the solution at this stage and in any case H_2S must be expelled.

Reagent: Acidify with acetic acid and evaporate to about 10 or 15 c.c.

This expels H_2S . To the solution add 5 c.c. NH_4Cl solution and make distinctly alkaline with NH_4OH . Boil and then add $(\text{NH}_4)_2\text{CO}_3$ solution until precipitation is complete. Allow to stand for five minutes. Filter.

Ppt. may contain carbonates of Ca, Sr and Ba.* Wash well with hot water. Pour a little warm HAc on to the ppt. on the filter. Test a small portion of the filtrate with K_2CrO_4 . If there is a ppt. treat the whole with K_2CrO_4 so as to remove Ba as BaCrO_4 . If there is no ppt. treat as filtrate below.

<i>Residue from K_2CrO_4 treatment: flame test will confirm Ba (light green).</i>	<i>Filtrate: May contain Ca^{++} and Sr^{++}. Divide into two parts:</i>
	<i>(a) Add CaSO_4 solution¹³ and boil. Faint ppt. indicates Sr^{++}.</i>
	<i>(b) If Sr^{++} present add dilute H_2SO_4, boil, filter and reject ppt. To filtrate add excess NH_4OH and ammonium oxalate solution white ppt.: Ca^{++}. If Sr^{++} absent treat solution as filtrate.</i>

* The reason why MgCO_3 is not precipitated was given on p. 21 (footnote).

Group VI. Magnesium, Sodium and Potassium.

If Ca^{++} was present in Group V add a little ammonium oxalate solution to the filtrate.²⁶ Boil and filter off the pptd. calcium oxalate. Omit this if Ca^{++} was not present. Divide solution into two unequal parts.

<i>(a) The smaller part: Add NH_4OH and NaH_2PO_4 solution. Shake well and allow to stand. White ppt.¹⁴ (may be hastened by scratching with glass rod) indicates Mg^{++}.</i>	<i>(b) The larger part: Evaporate to dryness in an evaporating basin and heat the residue until all fumes of NH_4 salts are expelled. (Fume chamber.) If there is no solid residue Na^+ and K^+ are absent. If there is a solid residue add 2 or 3 c.c. of water and filter if Mg^{++} is present. Divide the filtrate into two parts and test for Na^+ and K^+ using the tests given on p. 30.</i>
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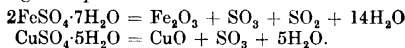
Notes on the foregoing Tables

The numbers correspond with those given against certain tests.

NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$, Hg_2Cl_2 and HgCl_2 and As_4O_6 are the commonest compounds to sublime.

e.g. $7\text{Na}_2\text{C}_2\text{O}_4 = 7\text{Na}_2\text{CO}_3 + 3\text{CO} + 2\text{CO}_2 + 2\text{C}$
but note $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$

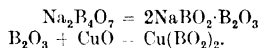
This requires high temperatures in some cases.



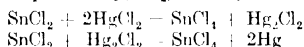
e.g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} = \text{Mg}(\text{OH})\text{Cl} + \text{HCl} + 5\text{H}_2\text{O}.$

The initial reaction is the formation of the carbonate of the metal. Excepting those of the alkali metals the carbonates are then decomposed to the oxide. This may be reduced but incrustations are obtained when the oxide is volatile at the temperature attained.

The metaborates are formed :

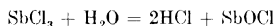


The blackening is due to the liberation of mercury. The compound $\text{Hg}(\text{NH}_2)\text{Cl}$ is also formed :



⁹ The milky ppt. is the oxychloride BiOCl produced by hydrolysis (cf. note 10).

¹⁰ The chloride is partially hydrolysed and the sparingly soluble oxychloride is formed :



¹¹ The conditions are chosen so as to favour the precipitation of hydroxides with low solubility products only. Compare the following values :

$[\text{Fe}^{+++}] [\text{OH}^-]^3$	1.1×10^{-36}
$[\text{Al}^{+++}] [\text{OH}^-]^3$	8.5×10^{-23}
$[\text{Cr}^{+++}] [\text{OH}^-]^3$	2.9×10^{-29}
$[\text{Ni}^{++}] [\text{OH}^-]^2$	8.7×10^{-19}
$[\text{Co}^{++}] [\text{OH}^-]^2$	1.6×10^{-18}
$[\text{Mn}^{++}] [\text{OH}^-]^2$	4.0×10^{-14}
$[\text{Zn}^{++}] [\text{OH}^-]^2$	1.0×10^{-18}
$[\text{Mg}^{++}] [\text{OH}^-]^2$	3.4×10^{-11}

This separation is possible through the use of NH_4OH in the presence of NH_4Cl (see p. 15).

If organic acids are present, when the strong acid is neutralised by the addition of ammonium hydroxide, metals of later groups may be precipitated since salts like calcium oxalate are soluble only in strongly acid solution. It is therefore essential to destroy organic acids before attempting Group III. Furthermore, certain metals, e.g. Fe^{+++} , which should be precipitated in Group III, form soluble complex salts with certain organic acids and would thus escape detection. Phosphate interferes with the group separation for a similar reason: the phosphates of later metals would be precipitated when the solution is made alkaline.

¹² This is an alternative way of performing the cobalt nitrate test (on the charcoal block). "Rinman's green" is formed. It consists of a solid solution of CoO in ZnO.

¹³ This distinction rests on the difference in the solubility products:

$[Ca^{++}][SO_4^{--}]$	2.3×10^{-4}
$[Sr^{++}][SO_4^{--}]$	3.6×10^{-7}
$[Ba^{++}][SO_4^{--}]$	1.2×10^{-11}

¹⁴ The ppt. is magnesium ammonium orthophosphate, $Mg(NH_4)PO_4$.

¹⁵ The ppt. is the compound $K_2Na[Co(NO_2)_6]$, potassium sodium cobaltinitrite.

¹⁶ The ppt. is the compound $Na_3H_2Sb_2O_7$, sodium dihydrogen antimonate.

¹⁷ e.g. $HCOONa + H_2SO_4 = NaHSO_4 + CO + H_2O$ "

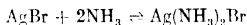
oxalates: $H_2C_2O_4 = CO_2 + CO + H_2O$

tartrates: $H_2C_4H_4O_6 = CO_2 + CO + 2C + 3H_2O$

¹⁸ $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 = 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$

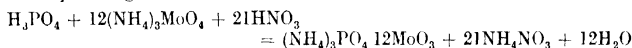
¹⁹ The blue "perchromic acid" is thought to be the oxide CrO_5 . The blue colour is developed only in acid solution.

²⁰ Ammonia solution reacts to form $Ag(NH_3)_2Cl$. Silver bromide forms a corresponding compound but the equilibrium:



does not lie so far to the right. Silver iodide is only very slightly soluble in ammonia solution.

²¹ The equation given for the reaction is:



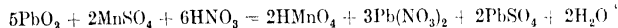
²² The brown compound has been given the formula $[Fe(NO)]SO_4$. The test is unreliable in the presence of bromide, iodide, nitrite and chromate.

²³ Alternatively the sodium aluminate solution may be boiled with some solid NH_4Cl . The hydrolysis:



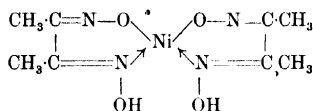
may be made to proceed to completion under these conditions since NaOH is removed to react with the ammonium chloride to liberate ammonia.

²⁴ A large excess of red lead (or lead peroxide) is essential for the successful performance of this test and even so the colour of the permanganic acid may be difficult to see:



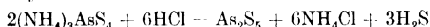
A much better method is to employ sodium bismuthate ($NaBiO_3$ —but composition variable). A little of the manganese salt solution is very greatly diluted to make 100 or 200 c.c. About 1 gm. of sodium bismuthate is then stirred in. The mixture is brown. On adding concentrated nitric acid, while stirring, the dark purple colour of permanganic acid is immediately seen. These conditions must be followed carefully. If too strong a solution of manganese salt is used the permanganic acid is immediately reduced and nothing but manganese dioxide is obtained.

- ²⁵ The red ppt. is the nickel derivative of dimethyl glyoxime and has the formula :



It is interesting that cobalt does not behave in the same way. The dark red-brown compound formed between a cobalt salt and α -nitroso- β -naphthol is a 6-co-ordinated compound. Cobalt salts are easily recognised through the colour change (red to blue) on adding excess of concentrated hydrochloric acid to a dilute solution. This change may be due to either (a) a change in the hydration of the Co^{++} ion or (b) the formation of a complex anion $[\text{CoCl}_4]^{-}$.

- ²⁶ If this is not done traces of Ca, Sr or Ba may give misleading precipitates. The carbonates of these metals are slightly soluble in ammonium carbonate solution.
- ²⁷ The basis of this separation is the formation of thio-salts by the sulphides of As, Sn, and Sb. The change depends on the acidic character of these sulphides which resemble the corresponding oxides. At the same time the excess sulphur present in ammonium sulphide causes oxidation.
- ²⁸ The treatment of a solution of these thio-salts with HCl causes the precipitation of the higher sulphide. This reaction may be compared with the liberation of an acid anhydride when the acid itself is unstable.



in the case of antimony there is no pentasulphide and the compound Sb_2S_4 is formed! Bismuth differs from the other elements in its sub-group of the Periodic Table in being altogether more metallic. It shows little tendency to assume a valency greater than three and no thio-salt is formed.

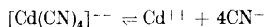
- ²⁹ Cu and Cd both form complexes :



In the case of copper the basic salt is first formed and this redissolves in excess NH_4OH :



- ³⁰ When KCN is added to a solution containing Cu^{++} and Cd^{++} ions, complex cyanides are formed in each case, the formulae being $\text{K}_3[\text{Cu}(\text{CN})_4]$ and $\text{K}_2[\text{Cd}(\text{CN})_4]$. Of these the former is much more stable. In the case of the cadmium compound, sufficient of the simple Cd^{++} ions are present at equilibrium :



for the sulphide to be precipitated on passing H_2S . In the case of the copper compound so little Cu^{++} ion is present that the solubility product of the sulphide is not reached.

- ³¹ SnS is not precipitated if the H^+ ion concentration is at all high. Sb_2S_3 on the other hand is precipitated from fairly acid solution. This explains the use of oxalic acid solution in this case.

QUANTITATIVE ANALYSIS

VOLUMETRIC ANALYSIS

Volumetric analysis is essentially the analysis of substances by means of changes which take place quantitatively in solution. The process of adding one solution gradually to a known volume of another so as to bring a definite chemical change exactly to completion is termed a titration. It follows that for a reaction to form the basis of a volumetric method it must proceed in accordance with the chemical equation representing the change and it must take place rapidly in dilute solution. Moreover, some means must be available for determining when sufficient of one reactant has been added to react with the other so that neither is then in excess. It should be clear also that the conditions must be such that for all practical purposes the change is non-reversible. The *end point* may be determined easily if it is marked by a change in colour due to the change of one of the reactants (e.g. as in titrations using potassium permanganate), but in general no such colour change occurs and an *indicator* must be used. The choice of an indicator is discussed later.

It will be obvious that we need at the beginning some solutions, the compositions of which are accurately known. Such solutions, which are employed to determine the composition of others by titration, are called *standard* solutions. For the preparation of a standard solution by weighing out a definite quantity of a substance the latter must be a compound of reliable composition and obtainable in a state of great purity. "*A. R.*" (Analytical Reagent) chemicals are sold under this designation when they conform to a published standard of purity and these are almost invariably used in making up standard solutions by direct weighing. A substance suitable for such work is called a *primary standard*. How the strength of the solution is stated is a matter of convenience; it may be given in grams of solute per litre or, more often, as a Normality or Molarity.

A *Molar* solution is one which contains one gram-molecular weight of solute in 1 litre of solution (written M). A 0.1 M solution will therefore contain one-tenth of the gram-molecular weight in 1 litre.

A *Normal* solution is one which contains one gram-equivalent of the solute in one litre of solution. This is for most purposes a more convenient system, but it cannot be used if the definition of the equivalent is at all equivocal. It must be remembered that the calculation of the equivalent must depend on the reaction involved. Consequently Normalities find their most simple application in the titrations of acids and alkalis.

The unit of volume. In the first part and in later parts of this book the metric unit of volume is written c.c. since it has long been customary to express volumes in this way. Recent determinations of the density

of water have, however, shown that 1 c.c. is not exactly the volume of a gm. of water at 4° C. (i.e. the units of mass and volume have not been related as was originally intended). Since the unit of mass is the standard kilogram and 1 litre of water at 4° C. is the volume having this mass it follows that 1 millilitre (*ml.*) of water at 4° C. does weigh 1 gm., whereas 1 c.c. weighs very slightly less. The relation between the two units is that

$$1 \text{ ml.} = 1.000027 \text{ c.c.}$$

For ordinary work such a difference is negligible, but since laboratory glass ware is now graduated in *ml.* this symbol is used throughout the present section.

Weighing. A brief note on this subject is included since no procedure can occupy so excessive an amount of time if a good method is not adopted. The student is advised to concentrate on making himself both quick and efficient by training himself carefully from the beginning. The following rules should be observed :

1. The balance should be checked before use to see that
 - (a) It is standing with the base in a perfectly horizontal position (plumb line or spirit level in the balance case). Unless the balance has been moved this adjustment will have been made.
 - (b) When released it swings an equal number of divisions on each side of the central position.
 - (c) The rider, if any, is at the 0 position of the rider scale.
2. No chemical substance is placed direct on the balance pan : a clean weighing bottle (p. 49), watch glass or aluminium scoop must be used. The weight of the substance is found by difference.
3. Weights are handled with tweezers and are never touched with the fingers. Nothing is placed on a balance pan or removed from it while the balance is swinging.

The object to be weighed is placed on the left-hand pan and a weight, judged to be too heavy, placed on the other. The left hand is now kept on the control knob of the balance while weights are moved with the right. In this way the balance may be quickly released into the swinging position immediately a new weight is added, and it may usually be seen *at once* if the total weight is too heavy or too light. This is important since, if more weights are needed, the control knob is turned back without a moment's delay into the resting position. All but the final adjustment of the smallest weights or the rider is then carried out in an extremely short time. The left hand should stay on the control knob and the box of weights be in such a position that the movement of the right hand is quick and easy.

The weight of the object has been found when the balance pointer moves an equal number of divisions on each side of the midpoint in two consecutive swings. The weight is then written down immediately in the laboratory notebook and checked as the weights are returned to the

box, starting with the largest. It is undesirable to enter records of this kind on pieces of paper.

The preparation of solutions. The weighing out of a substance preparatory to making up a solution may be quite approximate (e.g. to the nearest 0.5 gm.) if the solution is afterwards to be standardised by titration. The solutions used as primary standards are, however, made up by accurately weighing out a substance of great purity and known composition. The substance must be dry, and it is customary to use a weighing bottle fitted with a ground glass stopper. A weighing bottle is a necessity when the substance to be weighed is deliquescent or oxidises in air. The bottle is weighed when fairly full and then small quantities are tipped out into a clean dry beaker until a suitable amount has been weighed out. The exact weight is then obtained by difference. The alternative, sometimes employed, is to weigh the solid on to a tared watch glass or a small metal scoop. When not in use weighing bottles are kept in a desiccator.

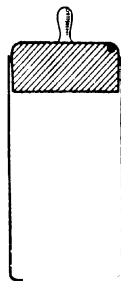


FIG. 1.

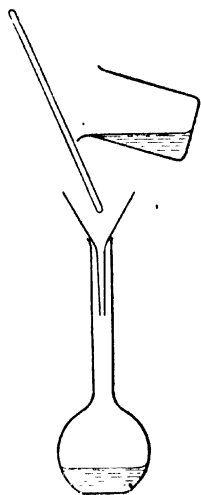


FIG. 2.

The procedure followed in weighing is described on p. 48. At this stage it will usually be sufficient to weigh substances no more accurately than to the third place of decimals. The other processes of elementary analysis are not of sufficient accuracy to justify a greater accuracy (and greater time) in weighing.

In dissolving up the weighed solid, heating should not be resorted to unless this is absolutely necessary on grounds of time. It is in any case unwise to heat strongly and still less to boil. Beakers should not be filled to more than two-thirds of their capacity, and if heated, half full is sufficient. It is very undesirable to have to transfer a solution from one beaker to another when making up a standard solution, not one drop of which must be lost in the process.

Transferring the cold solution to the graduated flask is a step requiring especial care. A loose-fitting glass funnel is placed in the neck of the flask and the solution is then poured down a glass rod into the funnel (Fig. 2). The rod serves the purpose of preventing the last drop from trickling down the outside of the beaker when it is set down. The beaker has, of course, to be thoroughly rinsed with distilled water, using a wash bottle. The walls of the beaker are washed down with small quantities of water and each is then transferred to the flask in the above manner.

When several such washings have been performed and each transferred, the volume of the solution is made up to the mark, using a pipette full of water to add the last few drops.

Pipettes. These are graduated in c.c. or ml. They are made to deliver the stated volume and no attempt should be made to remove the residual drop of solution when they have been emptied.

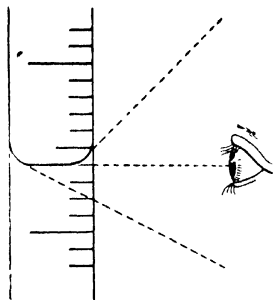


FIG. 3.

Burettes. These are filled by means of a funnel and then a little of the solution is run out before use so that the nozzle of the burette remains full. It is unnecessary always to commence a titration from the zero mark. In reading a burette the eye must be on the level of the bottom of the meniscus to avoid the error of parallax. In Fig. 3 the correct reading is 10.6 ml. and not 10.5 or 10.8 ml.

Cleaning and rinsing. While beakers and flasks in which standard solutions are made up must be clean and dry (or wet with distilled water only) pipettes and burettes must not be filled before they have been

- (a) Washed thoroughly clean,
- (b) Rinsed out with a little of the solution to be employed.

Titrimations. Titrimations may be carried out in conical flasks or beaker-flasks. Ordinary beakers are somewhat wide, and it is easy to lose a drop of solution when stirring or shaking. If vigorous shaking is necessary during the titration a stoppered bottle should be used.

It is very desirable to record actual burette readings when working. Usually the first titration will be somewhat rough since the position of the end point will not be known. Three accurate titrations should be performed in addition, and of these two should agree to within ± 0.1 ml. There are experiments for which this standard is too high, and in this case the arithmetic mean of several results should be taken. It is, of course, no use taking the mean of results which vary very erratically. The results are clearest when shown in the form of a table, e.g.:

Titration.	Burette readings.		Volume of acid used.
	From	To	
1	0.0	23.3	23.3 ml.
2	23.3	46.5	23.2
3	0.5	23.7	23.2

Volume of alkali used: 25 ml.

ACID-BASE TITRATIONS

Definitions. The student's attention is drawn to the definitions of acid and base given by Brønsted and Lowry. The more common definition of an acid is that it is a compound containing hydrogen which can yield hydrogen ions (more correctly oxonium ions H_3O^+) when dissolved in water. The essential condition is that the acid should be capable of providing the bare H^+ ion or proton. For this reason it may be defined simply as a proton donor. The corresponding definition of a base is that it is any substance which will function as a proton acceptor, i.e. remove hydrogen ions from an acid. This view necessitates certain changes in the classical viewpoint.*

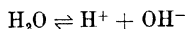
Basicity. The basicity of an acid is the number of hydrogen ions which can be formed from one molecule of the acid. The basicity must be known in order to calculate the equivalent of an acid since the latter is defined as the number of parts by weight which contain one part by weight of ionisable hydrogen. It follows that

$$\text{Equivalent of acid} = \frac{\text{Molecular weight}}{\text{basicity}}$$

A substance like sodium bisulphate, NaHSO_4 , is accordingly regarded as a monobasic acid when it is made to react with an alkali.

Neutrality and the Use of Indicators.

The idea of chemical neutrality is based on the properties of water. A solution is neutral (at 25°) when the hydrogen ion concentration is 10^{-7} gram-equivalents per litre, viz. the value it has in pure water. The ionisation of water:



or, more correctly:



provides one OH^- ion for every hydrogen ion formed. It follows that $[\text{OH}^-] = 10^{-7}$ gm. equivs. per litre also and that the ionic product

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

The hydrogen ion concentration is commonly expressed on the logarithmic scale due to Sørensen. Taking logarithms of the equation:

$$\begin{aligned} [\text{H}^+] &= 10^{-7} \\ \log_{10} [\text{H}^+] &= -7 \end{aligned}$$

whence $-\log_{10} [\text{H}^+] = 7$, and this is termed the *pH* for water. For 0.01N. HCl , we have $[\text{H}^+] = 0.01$ and hence $\text{pH} = -\log_{10} \text{H}^+ = 2.0$. For 0.01N. NaOH (assuming complete dissociation) $[\text{OH}^-] = 0.01$.

$$\text{Now} \quad [\text{H}^+] = \frac{[\text{H}^+][\text{OH}^-]}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

$$\text{and} \quad \text{pH} = 12.$$

* See *Chemical Reviews* (1928) for the original account by Brønsted.

It is an important rule that whatever the pH may be, for an aqueous solution, the ionic product K_w (at 25°) is maintained at 10^{-14} . This is because there is an equilibrium in which great reserves of unionised water molecules can be drawn on.

When equivalent amounts of acid and alkali are mixed the resulting salt solution may or may not have a pH value of 7. The reason for this has been given on p. 15: when one side of the salt is weak there is a certain amount of hydrolysis. When we talk of making such a salt by neutralising the acid with the base the term neutralisation is used in a somewhat loose manner. The term is retained, however, since in many cases it is possible to find an indicator which will change colour when the

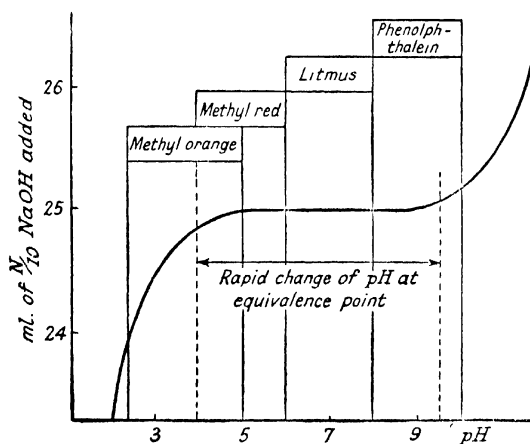


FIG. 4.

hydrogen ion concentration changes at the equivalence point (see below). The solution, at the midpoint of this colour change, is said to be "neutral" to the indicator selected. It would not be "neutral" to any indicator.

During the titration of a strong acid with a strong alkali the change of pH near the equivalence point is very rapid, as is shown by the graph. This represents the change of pH as $\frac{N}{10}$ caustic soda is added to 25 ml. of

$\frac{N}{10}$ hydrochloric acid.

Any indicator which changes colour between two pH values which come within the range $pH = 4$ to $pH = 10$ will therefore give an accurate end point. Methyl red is clearly the most suitable of those shown in the figure. The rule is simply that the pH range of the indicator shall coincide with the flat part of the titration curve. For the titration of a weak acid

with a strong alkali (or vice versa) the flat part is much shorter and there is less choice of indicators. The following are in general use :

	<i>Colour change.</i>	<i>Takes place between pH :</i>
Methyl orange	orange-yellow-red	3.0-5.0
Methyl red	red-yellow	4.4-6.0
Litmus	red-blue	6.0-8.0
Phenolphthalein	non-red	8.3-10.0
Thymolphthalein	non-blue	10.0-11.0

The least quantity of the indicator which is convenient should be used since it requires some additional H^+ or OH^- ions to effect the conversion of one coloured form into the other. The colour of these compounds is now generally ascribed to resonance among the various "structures" (cf. Speakman, *An Introduction to the Modern Theory of Valency* (1943) for an introduction to this idea). The change in colour may be due, in addition, to a tautomeric change (see textbooks of Organic Chemistry). See p. 200.

Preparation of Some Primary Standards.

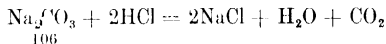
(a) Sodium carbonate Na_2CO_3 .

(b) Oxalic acid $H_2C_2O_4 \cdot 2H_2O$ or Succinic acid $H_6C_4O_4$.

(c) Hydrochloric acid from constant boiling hydrochloric acid.

It should be clear that after one or two of the above solutions have been made up by weighing out the solute, other acids and alkalis can readily be standardised by titration. Solutions are made up with distilled water in all cases and kept either in stoppered graduated flasks or transferred to clean dry stoppered bottles. A label showing the name of the solution, its strength and the date of preparation or of standardisation should be affixed.

(a) **Sodium carbonate.** The gram-equivalent of a base is that weight of it which reacts with 1 gram-equivalent of an acid, causing replacement of 1.008 gm. of hydrogen. From an equation it will be clear that when sodium carbonate is used as a "mild alkali" the equivalent is half the molecular weight (or, more correctly, the formula weight—there being no molecules of such compounds) :



One molecule neutralises two molecules of a monobasic acid. Since the molecular weight of anhydrous sodium carbonate is 106, the equivalent is 53.

5.3 gm. are required to make 1 litre of $\frac{N}{10}$ solution

13.25 gm. are required to make 250 ml. of N solution.

Using a weighing-bottle, the weight theoretically required will not be weighed out exactly. The solution must then be labelled with a factor

to express the concentration: 0.103 N can be expressed as $\frac{N}{10} \times 1.03$.

The weighing out of a required weight is in general slower and may be less accurate than weighing a quantity of about the required amount.

Pure dry sodium carbonate (A.R. standard) may be used in making the solution, but a good specimen of the carbonate may be made from sodium bicarbonate. The finely powdered bicarbonate is heated in a clean porcelain dish over a low flame for about twenty minutes. The temperature should not exceed 300°. The product can be tested for the presence of unchanged bicarbonate by heating a little in a dry test tube—CO₂ and moisture. The carbonate should be allowed to cool in a desiccator. Notes on the making of the solution have been given (p. 49).

(b) **Oxalic and succinic acids.** The procedure in the case of these two acids is the same. These organic acids suffer from certain disadvantages:

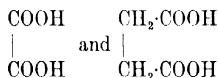
- (i) They must be dried over calcium chloride in a desiccator to constant weight without heating.
- (ii) They are weak acids and can be titrated against caustic alkali only, and
- (iii) Their solutions are a medium for the growth of certain bacteria, and thus after a few days have not the original composition.

Reagents of A.R. standard must be used. The equivalents are:

$$\text{Oxalic acid} \quad \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \quad \frac{126}{2} = 63$$

$$\text{Succinic acid} \quad \text{H}_6\text{C}_4\text{O}_4 \quad \frac{118}{2} = 59$$

Both acids are dibasic, as is shown by writing their formulae more fully:



Only the carboxylic hydrogen atoms are ionisable.

The solubilities are: oxalic acid hydrate 67.1 gm. per litre at 15° C., succinic acid 50.9 gm. per litre at 15° C. Decinormal $\frac{N}{10}$ solutions may therefore be readily made. Solutions of the sodium and potassium salts of these acids have a hydrogen ion concentration corresponding to pH of from 8 to 10, viz. on the alkaline side of neutrality. It will be seen (p. 52) that phenol-phthalein is a suitable indicator for use with these acids.

(c) **Hydrochloric acid from the constant boiling acid.** The strong mineral acids are never weighed out on an accurate balance for fairly obvious reasons. Advantage may be taken to make up hydrochloric acid as a primary standard from its constant boiling mixture with water. As shown in Fig. 5, the mixture containing 20.22 per cent. of hydrogen chloride has the highest boiling point (lowest vapour pressure)

and consequently by loss of more volatile component,* this is the final product of any distillation. Such a "constant boiling mixture" is given

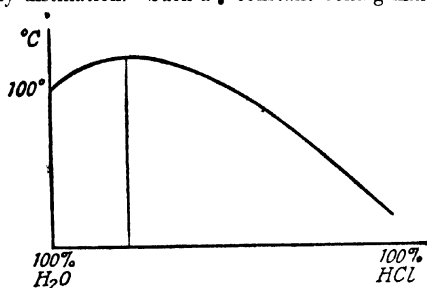


FIG. 5.

by several other acids (HBr 47.6 per cent., HI 58 per cent., HCOOH 77 per cent.).

<i>P</i> (cm. Hg.)	% HCl.	Weight distillate required for 1 litre Nacid.
72.0	20.315	179.460
73.0	20.293	179.555
74.0	20.269	179.766
75.0	20.245	179.979
76.0	20.221	180.193
77.0	20.197	180.407
78.0	20.170	180.650

Hydrochloric acid of density about 1.1 gm. per ml. should be distilled in a flask with a wide side arm and the last quarter of the distillate alone retained. The remainder, being of between 5N and 6N, is useful as ordinary bench dilute acid. From the height of the barometer the composition of the distillate retained may be found (see accompanying table).

* In weighing out the acid a clean stoppered conical flask of about 100 ml. capacity is used. This is weighed empty and then 80 or 90 ml. of the constant boiling acid are added and the flask re-weighed. Having recorded the weights the acid is run through a funnel into an approximately equal volume of water in a 500 ml. graduated flask. The conical flask and funnel are washed with another 100 ml. of water and the volume of the solution is then made up to 500 ml. with these washings and water. The normality of the acid is then calculated (see third column in table).

Litmus, or preferably methyl red, is used in the titration of hydrochloric acid with a strong alkali. Methyl red is much to be preferred for titrating the acid against ammonium hydroxide. For titration against sodium carbonate solutions methyl orange is used.*

* Screened methyl orange is easier to use since the colour change is more easily seen. This is a solution of methyl orange containing an inert dye, xylene cyanole; the colour change is from green (alkaline) to purple (acid), the neutral tint being grey ($pH = 3.8$).

If required an independent check on the strength of a solution of hydrochloric acid can be obtained by titrating with standard silver nitrate solution (see Volhard's method, p. 93).

The above method yields a solution of about N strength. If decinormal acid is required it should be made by taking 50 ml. in a pipette and making this up to 500 ml. in a graduated flask of this capacity.

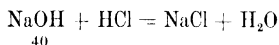
Other Standards. (a) Sulphuric Acid; (b) Caustic Soda.

(a) **Sulphuric acid.** When one volume of concentrated (96 per cent.) sulphuric acid is poured slowly into 30 volumes of distilled water, the mixture being kept well stirred, an approximately N solution of the acid is obtained. By dilution decinormal acid may be prepared. The titration of the acid against standard sodium carbonate is carried out with the use of methyl orange indicator.*

As in other cases of the sort, when exactly N or $\frac{N}{10}$ acid is required a solution which is slightly stronger is made. The strength of this is determined and it is then suitably diluted. Thus, if the Normality is 1.10, 1 litre of the solution will need to be diluted to make 1.10 litres.

Alternatively, $\frac{1000 \times 1.0}{1.10} = 909.1$ ml. should be made up to 1000 ml. by the addition of water. It may be mentioned that solutions commonly do not obey the "mixture law" exactly: there may be expansion or contraction on dilution. These effects are negligibly small when dilute solutions are employed, however.

(b) **Caustic Soda.** Sodium hydroxide, whether in sticks or pellets, contains small quantities of sodium salts and is extremely deliquescent. Solutions of strengths suitable for standardisation are therefore made up by rough weighing. N , $\frac{N}{2}$ and $\frac{N}{10}$ are concentrations commonly required. From the equation



it will be clear that caustic soda (a monoacid base) has an equivalent which is the same as the formula weight. The standardisation of the solution is carried out against a solution of standard acid of similar strength. Standard caustic soda solutions must be kept in stoppered bottles and out of prolonged contact with the air. Even so a solution which has been kept more than a week will need re-standardising. For carbonate-free alkali see p. 64.

Exercises in Acid-Base Titration

The calculations involved in volumetric analysis are generally very simple, and the student is left to work these out for himself. For acid-base titrations the equivalent of either the acid or the base is usually

* See note on previous page.

easily decided. Starting with some standard solutions there is, in general, no need to calculate the weight of a substance present in one litre of solution. x ml. of 0.95 N acid will clearly neutralise x ml. of 0.95 N alkali. If the alkali is not of the same normality, but is, for example, 1.1 N the result would be: x ml. of 0.95 N acid neutralise $\frac{0.95}{1.1} x$ ml. of 1.1 N alkali. A larger volume is clearly needed if the normality is relatively lower, and a smaller volume if it is higher. To calculate the weight of solute, per litre from the normality simply multiply by the equivalent.

1. Determination of Borax in a Solution.

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, gives a solution which is alkaline as a result of hydrolysis:



The boric acid formed is weaker than carbonic acid (the first stage dissociation constants are 6.6×10^{-10} and 3.04×10^{-7}) and the solution may therefore be used as an alkali just as sodium carbonate is used. When a strong acid is run in the neutralisation of the sodium hydroxide causes the hydrolysis to go to completion. Methyl orange is employed as an indicator. Standard hydrochloric, sulphuric or nitric acid may be used. The titration may be performed with either N or $\frac{\text{N}}{10}$ solutions.

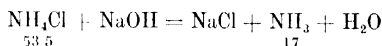
(19.1 gm. of the decahydrate gives an approx. $\frac{\text{N}}{10}$ solution of borax.)

Since it is really the sodium hydroxide, formed by hydrolysis, which is being titrated, the equivalent of borax is one-half of the formula weight. The weight of borax per litre can thus be calculated from the normality. By weighing out a known amount of the salt the percentage of borax may thus be found. Thus, if m gm. are used to make 1 litre of solution and by titration it is found that the solution contains x gm. there is $\frac{x}{m} \times 100$ per cent of borax in the sample.

Ordinary commercial borax contains sodium carbonate. To obtain the decahydrate in a reasonable state of purity two crystallisations from water are necessary. The salt readily effloresces to the pentahydrate and its use as a primary standard is therefore not convenient, at least for the beginner. In more experienced hands it is considered to be a better standard than sodium carbonate.

2. Determination of Ammonia in a Specimen of Ammonium Chloride. (See also method on p. 66.)

Method I. If heavy metals are absent the simplest method is to boil a weighed sample of the ammonium salt with excess of standard caustic soda. When all the ammonia has been expelled the remaining alkali is determined by titration with standard acid.



The analysis is carried out in duplicate. Two samples of the ammonium salt, about 1.5 gm. each, are weighed out from a weighing bottle or on to a scoop. They are placed in clean 150 ml. beakers which are clearly labelled A and B. Into each beaker 50 ml. of normal caustic soda is measured from a pipette. The strength of this alkali must be accurately known. The beakers are then covered with watch glasses of only slightly larger diameter.

The expulsion of ammonia is carried out by heating the beakers on the wire gauze until the contents boil gently. Small pieces of porous pot should be added to prevent bumping. After about quarter of an hour the hot solutions should not smell of ammonia, and if this is the case the solutions are allowed to cool, the sides of the beakers being washed with the jet of the wash bottle so as not to lose any caustic soda. Standard acid (N) is then run into each beaker in turn, methyl red or litmus being used to determine the end point. It should be clear that this titration must be done extremely carefully since a repetition of the whole experiment is undesirable.

The calculation of the ammonia present in the salt is done in two steps: (i) from the volume of standard acid calculate the volume of alkali actually used up in reacting with the ammonium salt; (ii) calculate from the equation how much ammonia would be liberated by the action of this volume of standard alkali. Clearly one litre of Normal alkali would liberate 17 gm. of ammonia.

If it may be assumed that no other ammonium salt or any other substance capable of reacting with caustic soda is present the percentage purity of the specimen may be calculated from the result.

Method II. When the salts of heavy metals are present the first method would be vitiated by the precipitation of hydroxides on adding caustic soda. A method capable of great accuracy in all cases is to boil a weighed specimen of ammonium salt with excess bench caustic soda and absorb the expelled ammonia in excess of standard (N) acid. The excess of standard acid is then determined by titration with standard $\left(\frac{N}{10}\right)$ alkali.

The apparatus is shown in Fig. 6. Simple precautions are taken to prevent splashing over of the alkali and the "sucking back" of the acid. About 1.5 gm. of the ammonium salt are accurately weighed out from a weighing bottle and transferred, with a little water, to the round flask which also contains a few pieces of porous pot. In the conical flask 50 ml. of N sulphuric or hydrochloric acid are placed, the volume being delivered from a pipette. The apparatus is then assembled and all joints made secure.

From the tap funnel about 100 ml. of bench caustic soda is then run in. The flask is then heated gently and finally boiled until the volume of liquid in the conical flask is about doubled. The connection at X is then broken before the flame is removed from under the flask. The solution

in the conical flask is then transferred with washings to a 250 ml. graduated flask and made up to this volume with distilled water. 25 ml. portions of the acid are titrated with decinormal alkali, using methyl red or litmus indicator.

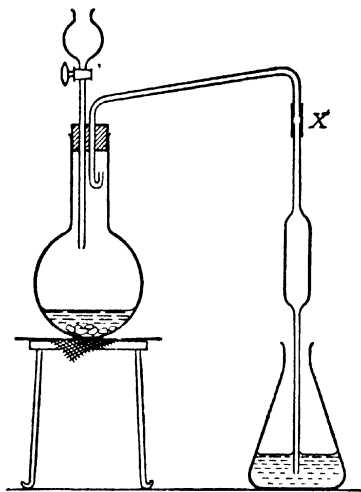
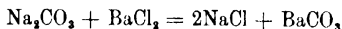


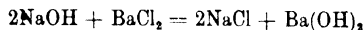
FIG. 6.

3. Estimation of Sodium Carbonate and Caustic Soda in a Solution containing both.

Method I. The best method of estimating these substances when present together in solution is to titrate the total alkali, using methyl orange indicator, and then to do a second experiment to determine the caustic soda alone. This is done by precipitating the carbonate by the addition of an excess of barium chloride:



The titration of the caustic soda is then carried out, using phenolphthalein as indicator. The reaction



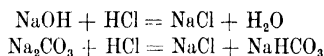
makes no difference to the result since the amount of OH^- remains unchanged.

(i) Titrate 25 ml. portions of the mixed alkali solution, using methyl orange indicator. The volume of N hydrochloric acid may be put equal to x ml. (If the alkali is sufficiently weak decinormal acid will be required.)

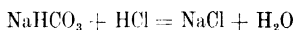
(ii) A fresh 25 ml. portion of the mixed alkali solution is placed in a conical flask and an approximately equal volume of barium chloride solution is added. Two or three drops of phenolphthalein are then added before standard acid is run in *slowly* from a burette. The

end point is reached before any barium carbonate is acted on by the acid. If y ml. of the acid are required on this occasion $(x - y)$ ml. must have been used to neutralise the carbonate present in the solution.

Method II. If standard hydrochloric acid is run into a cold solution of the mixed alkali in the presence of phenolphthalein indicator, the end point comes when all the hydroxide and *one-half* of the carbonate have reacted :



If methyl orange is now added to the colourless solution more acid may be added until a second end point is reached :



For accurate results by this method the solution of alkali should be kept near 0°C .; the addition of about 5 gm. of salt to the solution before titrating has also been recommended.

It follows from the equations that if 25 ml. of alkali require y ml. in the *second* titration, then $2y$ ml. if the amount of acid used up in the whole experiment in reacting with the carbonate present. If x ml. of acid were used in the first titration, $(x - y)$ ml. of acid reacted with the sodium hydroxide present.

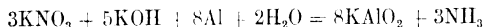
Note. A disadvantage of this method is the fact that in the titration using phenolphthalein the colour of the indicator dies away gradually instead of changing sharply from red to colourless. This is due to the slight buffer properties of bicarbonate solutions.

4. Estimation of the percentage of purity of a specimen of Potassium Nitrate by reduction with Devarda's Alloy and determination of the Ammonia produced.

Devarda's alloy has the composition Cu 50 per cent., Al 45 per cent. and Zn 5 per cent. It behaves like a zinc-copper couple and in the presence of aqueous electrolyte hydrogen is liberated. The reaction of the nascent hydrogen with potassium nitrate is :



The alloy is used in the presence of excess alkali so the change is represented more completely by the equation :



All the ammonia may be expelled from the solution by the action of heat. It is absorbed in a known amount of standard acid, and the excess acid is afterwards titrated.

The apparatus is the same as that shown on p. 59. Rubber stoppers should be used. Not more than 2 gm. of the nitrate is weighed into the half-litre round-bottomed flask. The receiver contains 50 ml. of standard $\left(\frac{N}{2}\right)$ sulphuric or hydrochloric acid. 50 ml. of bench caustic soda or

potash and about 3 gm. of Devarda's alloy are then added to the nitrate.

With the apparatus correctly assembled the temperature is raised *gradually*. Hydrogen and ammonia come off with much steam. Distillation is continued until the original solution is reduced in volume by about two-thirds. A drop of the residual liquid is then tested with Nessler's solution and no colour will be produced if all the ammonia has been expelled. At this point the connexion at *X* is opened before the flame is removed (the same precaution being necessary when doing the test with Nessler's solution). The contents of the receiver and pipette are thoroughly rinsed out and made up with washings to 250 ml. Standard alkali of $\frac{N}{10}$ strength is then used to titrate successive 25 ml. portions. Methyl red is the best indicator.

Having established the normality of the acid as x N, we have :

$$\text{number of equivalents of acid in 250 ml} = \frac{x}{4}.$$

Since the receiver originally contained 50 ml. of $\frac{N}{2}$ acid and this is $\frac{1}{40}$ th of an equivalent, it follows that the amount of acid used up in neutralising the ammonia is $\frac{1}{40} - \frac{x}{4}$, and this amount of acid would require the same number of equivalents of ammonia. The equivalent of ammonia is the same as the molecular weight, and thus $\frac{1}{40} - \frac{x}{4}$ gram-molecules of potassium nitrate must have been involved in the reaction. To get the weight of potassium nitrate in grams it is simply necessary to multiply by the molecular (or formula) weight.

5. Determination of Orthophosphoric Acid in a Solution.

The ordinary form of titration curve for a strong alkali and a strong monobasic acid is shown in Fig. 4. For a dibasic acid like oxalic acid* the titration curve shows two inflexions corresponding to the two stage dissociation (Fig. 7). For sulphuric acid, since the second dissociation is so strong in dilute solution, the curve is indistinguishable from that of a monobasic acid. In the case of orthophosphoric acid there are not three inflexions, as might be expected, but only two. This is because the salt K_3PO_4 is extensively hydrolysed. Titration to the point of its formation is therefore just as impossible as it is in the case of a salt of hydrocyanic acid. Either of the two inflexions shown in Fig. 8 can be found, the first by means of methyl orange and the second by means of phenolphthalein (or, better, thymolphthalein). The accuracy of the method is not as high as might be desired, but for many purposes, e.g. the preparation of the three different salts of the acid, it is satisfactory. The salts can be crystallised with a little difficulty.

A suitable solution of phosphoric acid can be made by roughly weigh-

* The first inflexion is of no practical importance in this particular case.

ing out the syrupy acid. The A.R. acid as sold has a specific gravity of 1.75 and is about 16 M. $\frac{M}{10}$ solution is required. Of this 25 ml. are

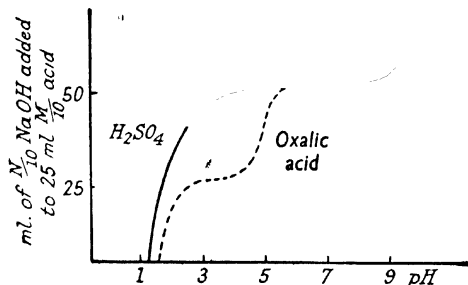


FIG. 7.

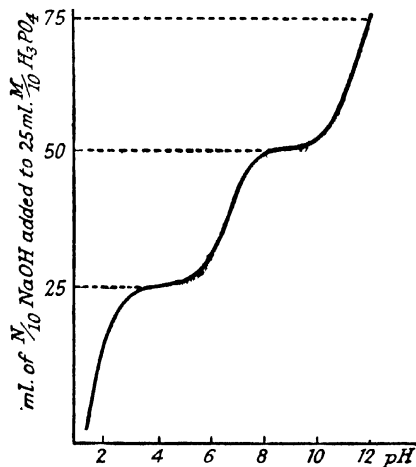
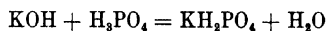


FIG. 8.

needed for each titration with $\frac{N}{10}$ caustic potash. The equations for the changes are :

(i) Methyl orange indicator :

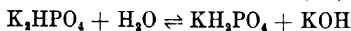


The end point is not very sharp. Screened methyl orange gives better results.

(ii) Phenolphthalein indicator (thymolphthalein is better) :



If this titration is performed 5 gm. of pure potassium chloride should be added to the acid before running in the alkali (or vice versa). The reason for this is that the salt K_2HPO_4 is partially hydrolysed :



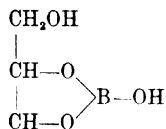
so that the solution is slightly alkaline unless the hydrolysis is repressed. This means that an incorrect end point is given.

More accurate methods of determining phosphate lie outside the scope of this book.

6. Titration of Boric Acid in the Presence of Glycerol or Mannitol.

Determination of Borate in a Sample of Borax.

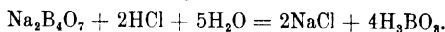
Boric acid, H_3BO_3 , is a tribasic acid. Only the first stage ionisation is appreciable. The dissociation constant, 5.0×10^{-10} , may be compared with the value for the first stage ionisation of carbonic acid: 3.04×10^{-7} . In the presence of glycerol or mannitol, however, it is found that a solution of boric acid is much more strongly acid. Against caustic soda it may now be titrated as a monobasic acid, the end point being given by phenolphthalein. The acid :



is thought to be formed in the presence of glycerol, but for practical purposes the reaction with alkali is represented :



The reaction is employed in this experiment to determine borate in a sample of borax, $Na_2B_4O_7 \cdot 10H_2O$. In the presence of acid, free boric acid is liberated from this salt (see p. 57) :



A titration is first necessary to obtain a neutral solution. About 30 gm. of the borax is weighed out and dissolved in water to make up one litre of solution. 50 ml. portions of this are titrated with $\frac{N}{2}$ hydrochloric acid, using methyl-red indicator. Omitting the indicator further 50 ml. portions are next neutralised with the $\frac{N}{2}$ acid and then treated with 50 ml. of neutral glycerol (the commercial product usually contains a little acid) or 1 gm. of mannitol. The solution is then titrated in 20 ml. portions with $\frac{N}{10}$ caustic soda, using phenolphthalein. It is essential to add a little more glycerol or mannitol at the end to ensure that the change is complete. If this causes the colour of the indicator to vanish more alkali is run in and then a further test with more glycerol or mannitol is made.

From the normality of the solution with respect to metaboric acid, HBO_2 , it is simple to calculate the percentage of B_2O_3 radical in the original borax. A litre of solution which is Normal with respect to HBO_2 is equivalent to a litre of $\frac{M}{4}$ borax solution.

Carbonate-free Sodium Hydroxide Solution

It has been mentioned (p. 56) that a solution of caustic soda cannot be kept more than a week without restandardising. Solutions made up in the ordinary way invariably contain a small amount of sodium carbonate, and for many purposes, e.g. stand-

ardisation of strong acids, this is not of great importance. For the titration of weak acids using phenolphthalein, however, such a solution is unsuitable.

Carbonate-free alkali is made from the best quality caustic soda sticks, rinsed quickly with water and dissolved in boiled distilled water. The solution is allowed to cool in a flask fitted with a soda-lime tube. The solution is standardised against oxalic acid. By doing parallel titrations, one in the cold and the other in boiling solution, using phenolphthalein, freedom from carbonate can be checked at any time. The two results should agree to within 0.1 ml. Carbonate-free alkali must be stored in an aspirator fitted with a soda-lime tube.

Use of Barium Hydroxide Solution.

The use of barium hydroxide is frequently preferred to the use of carbonate-free sodium hydroxide solution. The cold saturated solution is about 0.4 N and any carbonate formed settles quickly to the bottom as a sparingly soluble solid.

50 gm. of the crystals, $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, are added to 500 ml. of boiling distilled water. After a few minutes at the boiling point the mixture is allowed to cool in a flask fitted with a soda-lime tube. The cold saturated solution is decanted into an aspirator, connected as shown, with a special burette and carrying a soda-lime tube (Fig. 9). 1½ litres of cold boiled distilled water are then added so that the solution is made approximately decinormal.

In time a little turbidity is always noticeable in the baryta solution. This, however, settles to the bottom and the solution run to the burette should be clear. The solution must, however, be standardised against oxalic acid or hydrochloric acid on the same day as it is used. If hydrochloric acid is used the indicator is methyl red.

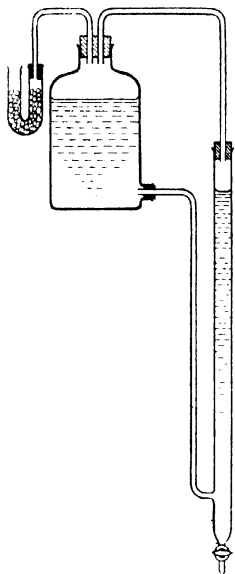
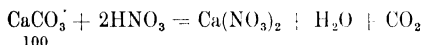


Fig. 9.

Additional Exercises

1. Standardisation of hydrochloric or nitric acid by means of calcite. 2 or 3 gm. of small calcite crystals are introduced into a clean beaker of 250 ml. capacity. The whole is then weighed and 50 ml. of roughly N acid are run in. The reaction is allowed to go to completion. The beaker is then placed over a flame and the solution boiled to expel dissolved carbon dioxide. The clear solution is then decanted and the beaker and residual calcite washed thoroughly with distilled water. After drying in the steam oven the beaker and contents are again weighed.

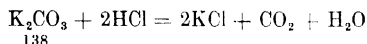
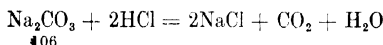


From the equation 100 gm. of calcite require 2 litres of N acid. If x gm. of calcite were used up $\frac{x}{100}$ 2000 ml. of N acid would be required. Since 50 ml. of acid were actually used, the concentration as a Normality is obtained by dividing.

2. Standardisation of approximately decinormal potassium hydroxide by means of pure potassium quadroxalate. This salt, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is a molecular compound of the salt KHC_2O_4 with the acid. The formula weight is 254. In titration three atoms of hydrogen in the molecule are replaced and hence the equivalent is 84.67. About 8.5 gm. are accurately weighed out to make up 1 litre of decinormal solution, the normality factor is then calculated.

The titration with potassium hydroxide is carried out precisely as for oxalic acid or succinic acid, using phenolphthalein as indicator.

3. Estimation of sodium carbonate and potassium carbonate in a solution containing both. For this exercise a solution containing about 15 gm. of the mixed anhydrous carbonates in 500 ml. is suitable. 25 ml. portions of this are titrated against $\frac{N}{2}$ hydrochloric or sulphuric acid, using methyl orange indicator. The interest of the exercise lies in the calculation.



Suppose that 1 litre of carbonate solution contains 30 gm. of the mixed carbonates (x gm. of Na_2CO_3 and $(30 - x)$ gm. K_2CO_3) and that 25 ml. of the solution requires 27.5 ml. of $\frac{N}{2}$ acid,

i.e. 1 litre of carbonate solution $\equiv 1.1$ litres $\frac{N}{2}$ acid.

The equivalents are : $\text{Na}_2\text{CO}_3 : 53$, $\text{K}_2\text{CO}_3 : 69$

$$x \text{ gm. } \text{Na}_2\text{CO}_3 \equiv \frac{x}{53} \cdot 2000 \text{ ml. of } \frac{N}{2} \text{ acid}$$

$$(30 - x) \text{ gm. } \text{K}_2\text{CO}_3 \equiv \frac{30 - x}{69} \cdot 2000 \text{ ml. of } \frac{N}{2} \text{ acid}$$

But
$$\left(\frac{x}{53} + \frac{30 - x}{69} \right) 2000 = 1100$$

Hence the value of x may be found.

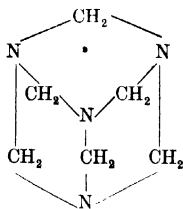
4. Determination of the amount of water of crystallisation in sodium carbonate crystals. A solution containing about 12 gm. of the crystals per litre is suitable for titration with $\frac{N}{10}$ acid, using methyl orange. This weight is accurately weighed out and 1 litre of solution made up (or 500 ml. containing 6 gm. may be sufficient).

If 25 ml. of the carbonate solution require x ml. of $\frac{N}{10}$ acid the normality of the carbonate is $\frac{x}{25} \cdot 0.1$ N. The weight of anhydrous carbonate is then $\frac{x}{25} \cdot \frac{1}{10} \cdot 53$ gm. per litre. If there are M gm. of the crystals in 1 litre

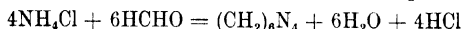
the amount of water in the crystals must be $M - \frac{53x}{250}$ gm. The weight of water combined with 106 gm. is then easily obtained. By dividing by the molecular weight of water the number of molecules of water combined with one molecule of the carbonate may be obtained. (By efflorescence washing soda crystals turn from the decahydrate to the monohydrate.)

5. Determination of the equivalent of magnesium. Some magnesium ribbon is first cleaned with sand paper, and two samples of about 0.5 gm. are accurately weighed out. Each of these is dissolved in 50 ml. of N hydrochloric acid or sulphuric acid in a conical flask. The excess acid is then titrated with standard alkali. The equivalent of the metal is the number of grams of it which react with 1 litre of N acid. The titration with the alkali should be accompanied by brisk stirring, and preferably is carried out at about 60°C . This is to avoid precipitation of the hydroxide during the titration. Methyl red is a suitable indicator.

6. Determination of ammonium chloride in a specimen with the use of formaldehyde. Ammonia and formaldehyde react to form hexamethylene tetramine $(\text{CH}_2)_6\text{N}_4$ with the structure :



If an ammonium salt is used the free acid is liberated in equivalent amount :



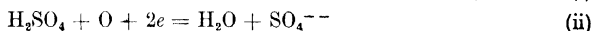
An approximately decinormal solution of ammonium chloride is first made by weighing out accurately about 5 gm. of the specimen and making 1 litre of solution. A quantity of 20 per cent. formaldehyde solution is then made neutral by adding a drop or two of phenolphthalein and then decinormal alkali, drop by drop, until a faint pink colour is obtained. 10 ml. of this solution are added to 25 ml. of the ammonium chloride and the mixture is then allowed to stand for two minutes. Standard (decinormal) alkali is then run in from the burette until the pink colour of the indicator is restored.

This is an accurate and rapid method of estimating ammonium salts. If pure ammonium chloride is used the method can be used to standardise an alkali without the use of standard acid.

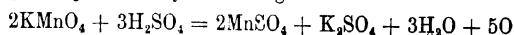
OXIDATION-REDUCTION TITRATIONS

Oxidation and reduction are two processes which have very wide application in analytical chemistry, wider, one would say, than that of acid-alkali titrations. It will be clear that if we are estimating a substance which is a reducing agent, e.g. a ferrous salt, all we have to do is to titrate its solution against a suitable oxidising agent in standard solution. In many cases it is more convenient to use an excess of the oxidising agent and then determine the excess by a "back-titration." For this a standard solution of a reducing agent will be necessary.

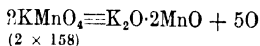
The gram-equivalent of an oxidising agent is determined, not by reference to any particular element which it contains, but by calculating how much of it is needed to oxidise 1.008 gm. of hydrogen to water. It is, of course, a simple matter to replace this "1.008 gm. of hydrogen" by "the equivalent of another element having regard to the change involved." Thus, in the change of ferrous iron to ferric the valency changes by one unit and the equivalent of ferrous iron is 56 (the atomic weight). Potassium permanganate in the presence of dilute sulphuric acid is often used to effect this change. We have then (cf. p. 10)



The oxygen is provided by the change:



or more shortly



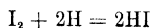
From equation (ii) it will be seen that the provision of five atoms of oxygen would accompany the taking up of ten electrons, and this brings about the oxidation of ten atoms of ferrous iron. The equivalent of potassium permanganate is then $\frac{316}{10} = 31.6$ (in *acid* solution).

The problem of finding an indicator for an oxidation-reduction titration is more complex than it is for acid-alkali titrations. Fortunately the problem is readily solved in a number of simple cases. There is as yet no general answer to this question, and advances in theory will probably revolutionise this type of work. In the case of potassium permanganate the reagent itself is strongly coloured and the colour pales sharply at the end point (Mn^{++} salts are in general pale pink). Iodine titrations are carried out with the use of starch as an indicator. As soon as any excess iodine is present it combines with the starch to form a dark blue adsorption compound of uncertain composition (at ordinary temperatures). It is obvious that a substance can be used as an internal indicator (i.e. placed in the titration vessel) only when it does not appropriate the oxidising agent until there is a slight excess. When such an indicator is not available it may be possible to test for the presence of unoxidised material. Thus, in one method of titrating ferrous salts with potassium dichromate, drops of the solution are withdrawn from the titration vessel at intervals and added to spots of potassium ferricyanide solution on a porcelain tile. A dark blue colour shows the presence of unoxidised ferrous salt. The employment of an external indicator has the disadvantages of being slow and not particularly accurate. The discovery that certain organic dyes can be employed as internal indicators for oxidation-reduction changes has greatly improved certain volumetric methods. The colour-change of the dye must not occur before the main oxidation change between the reactants has occurred, but it should then take place immediately and with as little excess of oxidising agent (or reducing agent) as possible. The theory of these indicators is still incomplete and lies beyond the scope of this book.

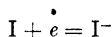
The oxidising action of potassium permanganate and potassium dichromate rests on the formation of compounds derived from lower oxides:

Oxidant.	MnO_4^-	Reduction product.	Mn^{++}
Corresponding oxide.	Mn_2O_3	Oxide.	MnO

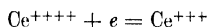
The oxidising action of iodine depends on the combination of the element with hydrogen:



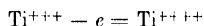
but the fundamental change is simply the change from the covalent to the electrovalent state :



That this is the essential process in oxidations involving ions is particularly clear in the behaviour of ceric salts which are very strong oxidising agents :



and in the behaviour of titanous salts which are reducing agents :



Both of these can be used in conjunction with such "redox" indicators as diphenylamine or methylene blue. Unfortunately their uses are restricted at present and the use of such indicators is only described in a few exercises in the following pages. For a note on oxidation-reduction potentials see Appendix II, p. 218.

POTASSIUM PERMANGANATE

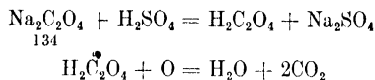
Preparation of approximately $\frac{N}{10}$ Potassium Permanganate Solution.

In the presence of dilute sulphuric acid and a reducing agent two molecules of potassium permanganate provide five atoms of oxygen. Potassium sulphate and manganous sulphate are formed. As explained on the previous page the equivalent of potassium permanganate, when used in acid conditions, is one-fifth of the formula weight.

A solution of about decinormal strength is commonly used. For this about 3 gm. of the crystals are weighed out, dissolved in about 200 ml. of warm distilled water, and then the volume of the solution is made up to one litre in the usual way. Potassium permanganate is not obtainable in the highest state of purity and solutions when made up have to be standardised. Standardisation should be carried out preferably after twenty-four hours. The standard solution should not be allowed to come into contact with rubber.

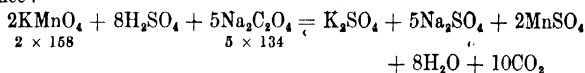
Standardisation of Potassium Permanganate with Sodium Oxalate (or Oxalic Acid).*

Standard sodium oxalate solution is first made up. Some pure (A.R.) sodium oxalate, dried in an air oven at about 110° C., is placed in a weighing bottle and about 3.5 gm. are accurately weighed out into a clean beaker of about 250 ml. capacity. The salt is dissolved in about 200 ml. of water and the solution is transferred with washings to a 500 ml. graduated flask. The equivalent is 67.



Alternative methods of standardisation are given afterwards.

Hence :



In doing the titration 25 ml. portions of the oxalate solution are diluted with about 100 ml. of water and about 5 ml. of concentrated sulphuric acid are added. The solution is then heated nearly to boiling and the permanganate is run in from a burette while stirring rapidly. The temperature should not be allowed to fall below 60° since the reaction is then slowed down inconveniently.

The first drop or two of potassium permanganate is decolorised slowly, but as soon as some manganous sulphate has been formed the reaction proceeds rapidly with the evolution of carbon dioxide. Manganous sulphate is a catalyst for the change. The end point is reached when a permanent pale pink coloration is obtained.

If insufficient sulphuric acid is present, or if the permanganate is run down the side of the titration vessel, a little hydrated manganese dioxide may be formed as a brown deposit or film. If this does not clear on adding a little more acid the titration must be rejected.

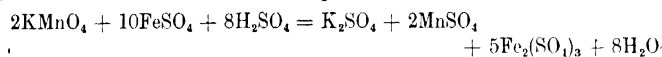
Notes.

1. If preferred the crystalline oxalic acid may be used in place of the sodium salt. In this case 3.15 gm. of the acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, are needed for 500 ml. of $\frac{\text{N}}{10}$ solution. The equivalent is 63. The procedure for the titration is the same as for sodium oxalate. The free acid does not always correspond exactly to the formula given owing to slight variation in the amount of water of crystallisation. Its solution keeps badly owing to the multiplication of bacteria.

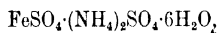
2. Standard permanganate solution should be kept in dark glass bottles. Some of its commonest uses are given below. It is not used for oxidation in acid solutions containing chlorides since it readily oxidises dilute hydrochloric acid.

Standardisation of Potassium Permanganate with Ferrous Ammonium Sulphate (Mohr's salt).

A solution of ferrous sulphate is oxidised by potassium permanganate solution in accordance with the equation :



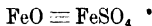
Ferrous sulphate crystals, however, always contain a small amount of the ferric salt produced by air oxidation, and the solution also is oxidised slowly in air. The double salt, ferrous ammonium sulphate,



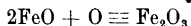
however, can be bought in a high state of purity. Alternatively the commercial product can be recrystallised from water. This salt and its

solution are comparatively stable in air. The stability of a solution of ferrous sulphate is increased by the addition of sulphuric acid, and this applies to the double salt (cf. p. 218).

From the above equation or from the relationships:



and



it is clear that the equivalent of ferrous sulphate is the formula-weight. Hence the equivalent of the double salt is 392, of which weight almost exactly one-seventh is iron. For 250 ml. of $\frac{N}{10}$ solution, therefore, 9.8 gm. of ferrous ammonium sulphate are needed. This quantity is accurately weighed out and 250 ml. of solution made up with the addition of plenty of bench sulphuric acid (say 50 ml.). If more or less than 9.8 gm. are used the normality is calculated. 25 ml. portions of the solution are acidified with about 10 ml. of bench sulphuric acid before titration with permanganate.

Standardisation of Potassium Permanganate by means of Iron Wire.

Ferrous sulphate may be made by dissolving very pure iron wire (1.4 gm. for $\frac{N}{10}$ in about 50 ml. of bench sulphuric acid. The solution must be kept strongly acid and is made up to a volume of 250 ml. in a graduated flask with sulphuric acid and water. It must be used immediately.

The method is open to the objection that iron wire always contains a little carbon and is never 100 per cent. iron.

EXERCISES EMPLOYING POTASSIUM PERMANGANATE

1. Estimation of Iron in a specimen of Iron Alum. Ferric salts can be estimated

- (a) by first reducing them in solution and titrating the ferrous salt with standard permanganate (or dichromate); or
- (b) by direct titration with a strong reducing agent such as titanous sulphate.

The first method is used here. For the use of titanous sulphate, see p. 73.

Iron alum has the formula $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. Since the equivalent of Fe^{+3} is 56 one litre of $\frac{N}{10}$ solution can be made by reduction of one-twentieth the formula weight in grams of the alum. About 12 gm. of the crystals, previously powdered in a mortar, are weighed out accurately and dissolved in not more than 150 ml. of water in a conical flask. This flask is then fitted with a Bunsen valve (Fig. 10) and a little granulated zinc, and about 25 ml. of concentrated sulphuric acid are then added.* The reduction may take about quarter of an hour. To see if it is complete

* While a Bunsen valve is convenient if the reduction is left overnight to go to completion, a long glass tube will prove just as useful and efficient in ordinary use. For an alternative method of reducing ferric salts see p. 76.

a drop of the solution is withdrawn on a glass rod and tested with potassium ferrocyanide on a white tile. More zinc may be needed to complete

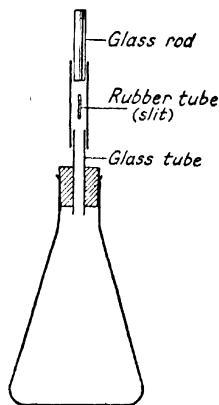
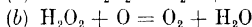
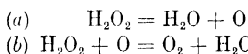


FIG. 10.

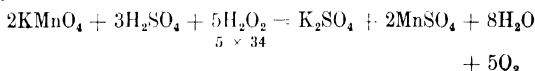
the reduction. When this is accomplished the cold solution is quickly filtered through glass wool in a funnel into a 250 ml. graduated flask. The volume is made up with bench sulphuric acid (50 ml.) and water, first used for washing out the conical flask.

25 ml. portions of the ferrous sulphate solution are next titrated with standard potassium permanganate in the usual way. From the fact that N Ferrous sulphate solution contains 56 gm. iron per litre it is easy to calculate the percentage of iron in the original salt. It is not admissible to use the result to calculate the percentage purity of the alum because of the other constituents which may vary a little from the theoretical composition. It would be desirable, for example, to determine the ammonium radical by Method II on p. 58.

2. Estimation of Hydrogen Peroxide in a solution. Hydrogen peroxide can behave as either an oxidising agent or a reducing agent depending on the nature of the substance with which it is in contact. These different behaviours may be represented:



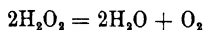
In the presence of permanganate in acid conditions the second reaction takes place:



"20 volume" hydrogen peroxide is about 4 N and contains about 6 per cent. of the compound. 25 ml. of this solution are pipetted into a 1 litre graduated flask and the solution made up to the mark with water. 25 ml. of this solution should be diluted with ten volumes of water and about 30 to 40 ml. of bench sulphuric acid added before doing a titration with standard permanganate. Three accurate titrations should be performed as usual.

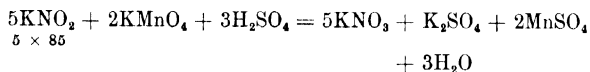
It will be clear from the above equations illustrating its behaviour, that as an oxidising agent or as a reducing agent the equivalent of hydrogen peroxide is one half of the molecular weight. By calculating the weight in grams per litre from the normality one can afterwards obtain the result as a percentage, remembering that the solution used was 40 times as dilute as the original solution marked "20 volume."

Alternatively the "volume strength" of the original hydrogen peroxide solution may be calculated. From the equation:



it is clear that one gram-molecule (34 gm.) of hydrogen peroxide can provide 11.2 litres of oxygen at N.T.P. If there are W gm. of the substance present in 1 litre each litre will provide $\frac{11.2 \times W}{34}$ litres of oxygen at N.T.P. This is the "volume strength."

3. Estimation of Sodium Nitrite in a solution. The estimation of nitrites as reducing agents is complicated by the fact that nitrous acid, liberated in the presence of acid, readily decomposes with evolution of oxides of nitrogen. In Lunge's method this difficulty is overcome by placing the nitrite solution in the burette and running it into warm acidified permanganate. The nitrous acid is then immediately oxidised to nitric acid. The equation for the change is:



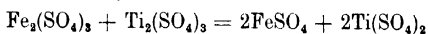
A suitable solution for the exercise may be made by dissolving about 4 gm. of sodium nitrite or 5 gm. of potassium nitrite in water and making the volume up to one litre. For determination of nitrite in a specimen it would be necessary to fuse in a covered crucible and allow the solid to cool in a desiccator. The sodium salt is very deliquescent.

In a titration 25 ml. of $\frac{N}{10}$ potassium permanganate are placed in a beaker, diluted to about 200 ml. with water, acidified with about 20 to 30 ml. of bench sulphuric acid and warmed to about 40° C. With the burette nozzle just below the surface of the permanganate, which is kept well stirred, the nitrite solution is run in slowly. The end point is reached when the permanganate is just decolorised. The result may be stated as a normality or in grams per litre of nitrite.

TITANOUS SULPHATE

Standardisation of a solution of Titanous Sulphate.

Titanous salts are among the most powerful reducing agents available in volumetric analysis. By means of titanous sulphate solution ferric salts can be estimated by direct titration:



Ferrous salts are relatively such weak reducing agents that the reduction goes to completion.

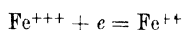
Commercially, titanous sulphate is available in a strong dark violet coloured solution. 100 ml. of this are mixed with 100 ml. of 50 per cent. sulphuric acid and brought to the boil in a flask. The solution is then diluted with about a litre of boiled water and kept in a stoppered bottle.

Titanous chloride is obtainable in a similar solution and can be made up instead. It is, however, much more readily oxidised by exposure to the air and must be kept under hydrogen. With reasonable precautions the sulphate can be used in an ordinary burette, but it must be standardised just prior to its use.

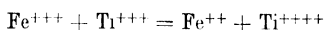
The quickest method of standardisation in the case of titanous sulphate is to employ standard permanganate. 25 ml. of about 0.1 N ferrous ammonium sulphate are titrated in the ordinary way with standard permanganate. 1 or 2 ml. of potassium thiocyanate solution are then added and titanous sulphate run in until the red colour is just discharged.

Estimation of Iron in Iron Alum by titration against standard Titanous Sulphate solution.

The equivalent of iron alum is one-half of the formula weight, as is evident from the change involved in its reduction :



The reaction with titanous salt may be represented :



the anions common to both sides of the equation not being shown. The titanous salt, by lowering the valency of the iron, is of course supplying electrons (p. 10). Since the formula weight of iron alum is 964, 12.05 gm. of it are needed to make 250 ml. of a decinormal solution. About 12 gm. of the powdered alum are accordingly accurately weighed out and the solution is prepared in the usual manner.

There are two methods available for performing the titration of the ferric salt with titanous sulphate :

(a) Using potassium thiocyanate indicator. 25 ml. portions of the alum solution are treated with a few ml. of potassium thiocyanate solution. The blood red colour of ferric thiocyanate persists until all the iron has been reduced to the ferrous state. This gives quite a sharp end point.

(b) Using methylene blue indicator. 25 ml. portions of the alum solution are treated with 2 or 3 drops of methylene blue solution made up in alcohol. When titanous sulphate solution is run in the blue colour disappears with the first drop in excess. The dye is decolorised owing to the formation of leuco-base. The end point is quite sharp (and reversible in direction) ; more accurate results are said to be obtained by warming the ferrous salt solution to about 40° C. before completing the titration.

POTASSIUM DICHROMATE

Preparation of approximately $\frac{N}{10}$ Potassium Dichromate Solution.

As an oxidising agent potassium dichromate possesses the advantages :

- (a) it is readily obtained in a state of purity and can, in fact, be weighed as a primary standard ;

Method I. Diphenylamine in sulphuric acid* used as indicator. Four drops of this indicator are needed, together with 5 ml. of phosphoric acid (made by diluting syrupy phosphoric acid with twice its volume of water). As potassium dichromate is run in the green colour deepens and then, at the end point, a blue colour is produced by the first slight excess of dichromate. 18° to 20° C. is a convenient temperature for obtaining accurate results.

Method II. Potassium ferricyanide used as an external indicator. The tests are carried out on a porcelain tile. After each addition of dichromate solution a drop of the well-stirred mixture is withdrawn on a glass rod and added to a spot of potassium ferricyanide solution, freshly prepared. As long as a dark blue precipitate is seen on mixing the drops some unoxidised ferrous iron must be present. At the end point there is no blue precipitate, but only a clear brown coloration. It is, of course, important to wash the glass rod between each test. The procedure is more troublesome than that of Method I; it is less accurate and open to the objection that there is some loss of solution.

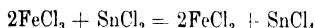
Estimation of Ferric Iron in Solution using Potassium Dichromate.

If a solution containing ferric iron is to be analysed with the use of dichromate, it is first necessary, as in using permanganate, to reduce the iron to the ferrous state. In this case zinc and sulphuric acid (p. 71) may not be a suitable reducing agent since zinc ions give a precipitate with the external indicator of potassium ferricyanide, and this 'obscures the end point. (This objection does not operate against the use of diphenylamine indicator.) There are, however, other methods of reducing ferric salts in solution, the best being to use stannous chloride solution as a reducing agent and to get rid of any excess by treatment with mercuric chloride solution.

It should be understood that the reduction may be carried out in the way described on p. 71, provided that potassium ferricyanide is not afterwards used as an indicator for the titration with dichromate.

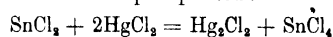
The reduction with stannous chloride proceeds rapidly and may conveniently be carried out with each successive 25 ml. portion of ferric salt solution. The latter should therefore be of about decinormal strength (5.6 gm. of iron per litre).

To 25 ml. of the ferric salt solution 2 or 3 ml. of concentrated hydrochloric acid are added and then the solution is warmed to 60° or 70° before adding stannous chloride drop by drop from the bench bottle. Enough stannous chloride must be added to remove the yellow colour of the ferric ion.



* The indicator solution is made by dissolving 0.2 gm. of diphenylamine in 100 ml. of concentrated sulphuric acid. Oxidation produces diphenylbenzidine and it is this which undergoes the colour change. In the absence of phosphoric acid, Fe^{+++} ions tend to produce the colour change (cf. Appendix II, p. 218). Still better is N-phenylanthranilic acid which is used in 1.3 N. H_2SO_4 . This gives a reddish purple colour at the end point.

Only a slight excess of stannous chloride should be added. The solution is then cooled under the tap and a slight excess of mercuric chloride solution added. This oxidises the excess stannous chloride, and white insoluble mercurous chloride is precipitated :

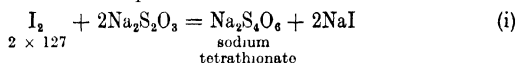


A slight white precipitate should therefore be obtained. If too much stannous chloride is present a heavy precipitate which turns grey or black will be obtained. The solution must in such a case be rejected. The mercurous chloride and excess of mercuric ion do not interfere with the subsequent titration with dichromate which is carried out in the usual way.

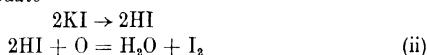
IODOMETRY

Titration involving iodine find wide application, and the method of estimating other substances by the use of iodine is termed iodometry. Standard iodine solution may be used to estimate reducing agents like sulphurous and arsenious acids; oxidising agents are made to liberate iodine from potassium iodide.

The strength of an iodine solution may be determined by titration with standard sodium thiosulphate solution:



but this substance is not a primary standard. It is accordingly necessary to begin by standardising the thiosulphate against potassium permanganate, potassium dichromate or potassium iodate. In all of these cases the process involves two steps: (1) the liberation of iodine from excess (acidified) potassium iodide by a known volume of standard permanganate, dichromate or iodate



and (2) the titration of this iodine against the thiosulphate solution (equation (i) above).

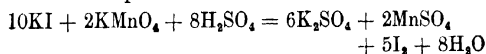
Since 16 gm. of oxygen are, by equation (ii), equivalent to 2×127 gm. of iodine, 1 litre of decinormal permanganate, dichromate, or iodate will liberate 12.7 gm. of iodine. This, in turn, will require 1 litre of decinormal thiosulphate. The calculation of the normality of a solution of thiosulphate is therefore straightforward. If 25 ml. $\frac{\text{N}}{10}$ permanganate are used and the iodine liberated requires 28 ml. of the thiosulphate the strength of the latter is $\frac{25}{28} \times 0.1 \text{ N}$.

Standard sodium thiosulphate solution is an essential accessory and is frequently employed to determine iodine liberated from potassium iodide by oxidising agents.

Standardisation of a Solution of Sodium Thiosulphate.

Approximately decinormal sodium thiosulphate is made by weighing out about 25 gm. of the salt, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, the equivalent of which is 248.2 (equation (i) above) and making one litre of solution. The methods of standardising against potassium permanganate and against potassium iodate will be given.

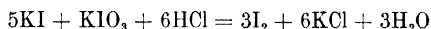
Method I. Using Potassium Permanganate. The complete equation for the reaction with potassium iodide is:



25 ml. of $\frac{N}{10}$ permanganate are placed in a beaker or beaker-flask, and the solution is made acid with bench sulphuric acid. About a gram of potassium iodide is added and the mixture is stirred. The purple colour of the permanganate is replaced by the brown of iodine dissolved in excess potassium iodide. The thiosulphate is then run in from a burette until the solution, which is kept stirred, becomes pale yellow. At this point, and not before, one or two ml. of freshly made starch solution* is added and the titration is continued until the dark blue colour of the starch-iodine compound is just removed.

The method of calculating the strength of the thiosulphate solution has been described.

Method II. Using Potassium Iodate. The equation for the liberation of iodine by this oxidising agent is:



Potassium iodate has the advantage that, unlike potassium permanganate, it can be made up in solution as a primary standard. It is obtainable pure, and its equivalent is one-sixth of its formula weight. Using $\frac{N}{10}$ solution the procedure for standardising thiosulphate is the same as with permanganate.

Standardisation of Iodine Solution with Sodium Thiosulphate.

This process has in all essentials been described already. An approximately decinormal solution of iodine is made by weighing out approximately 3.2 gm. and making up 250 ml. of solution with the addition of about 4 gm. potassium iodide. The thiosulphate solution is placed in the burette. 25 ml. portions of the iodine solution are placed in a conical flask and thiosulphate run in until the iodine solution becomes pale yellow. A little starch solution is then added, and the titration continued until the blue colour of the starch-iodine compound is just removed. Except when doing a titration the conical flask is kept stoppered on account of the vapour pressure of iodine.

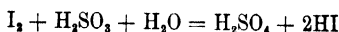
EXERCISES EMPLOYING TITRATION OF IODINE

1. Estimation of Sulphur Dioxide in a Solution. Although sulphurous acid is oxidised by iodine the direct titration is unsatisfactory,

* *Starch solution.* A little of a thin paste of starch and water is poured into 200 ml. of boiling water. The solution should then be only slightly opalescent. It is then boiled for about two minutes. The clear portion is decanted after the mixture has stood for a few minutes. This indicator solution does not keep more than twenty-four hours, since it usually becomes infected with a mould which liberates a hydrolytic enzyme.

To obtain consistent results the same volume of the same starch solution should be used throughout a series of titrations. The same number of drops should be used.

since the hydrogen iodide formed may reduce some of the sulphurous acid to sulphur. The reaction :



proceeds quite satisfactorily, however, if 25 ml. of the sulphurous acid are added to excess iodine solution. The excess may then be estimated by titration with standard thiosulphate. This must be done immediately, since hydriodic acid is oxidised by air.

To prepare a saturated solution of sulphur dioxide a bottle of the liquid should be connected to a glass tube ending in a jet at the bottom of a tall measuring cylinder containing water (50 or 100 ml.). A slow stream of small bubbles is then passed for at least an hour. When the solution is saturated the bubbles show no diminution in size and are not absorbed.

Such a solution is between 4 N and 5 N, and will require dilution to $\frac{\text{N}}{10}$ strength. The solution must not be left exposed to the air, since it oxidises.

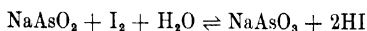
25 ml. of a solution of suitable strength are added to 50 ml. of $\frac{\text{N}}{10}$ iodine.

The unchanged iodine is then determined by titration with standard thio-sulphate in the ordinary way. It should be clear how the solubility at a given temperature can thus be determined.

2. Determination of Arsenious Oxide in a Specimen. Titration of Sodium Arsenite with Iodine. Arsenious oxide is only very slightly soluble in water, but it dissolves readily in a solution of sodium carbonate forming sodium arsenite.



About 5 gm. of the specimen are accurately weighed out and dissolved by heating in about 100 ml. of water containing 20 gm. of pure sodium carbonate. Since iodine reacts with sodium carbonate it is necessary to neutralise the excess. A drop of phenolphthalein is added, and then hydrochloric acid is run in drop by drop until the colour of the indicator is discharged. The solution is then diluted to fill a litre graduated flask. Iodine solution oxidises sodium arsenite to sodium arsenate :

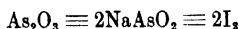


Since the change is reversible it is necessary to remove the hydriodic acid as it is formed. Sodium bicarbonate, present in excess, provides a suitable buffer for this purpose. In performing a titration, therefore, 25 ml. of the sodium arsenite solution are mixed with two or three grams of sodium bicarbonate and the mixture well stirred before running in the iodine.

In this estimation iodine solution is placed in the burette. A little starch solution is added to the sodium arsenite solution before starting the titration. One drop of iodine solution in excess produces a dark blue colour.

From the normality of the arsenite the weight of arsenious oxide in

one litre of solution by multiplying by the equivalent. From the relationships

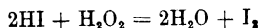


it will be evident that the equivalent of arsenious oxide is one-quarter of the molecular weight.

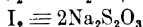
3. Iodometric estimation of Hydrogen Peroxide. A stronger solution of hydrogen peroxide than was used in the titration with potassium permanganate (p. 72) is needed in this experiment. The ordinary 20-volume solution is diluted to ten times its volume.

About 2 gm. of potassium iodide are dissolved in 200 ml. of water, and about 30 ml. of 50 per cent. sulphuric acid are added. This large excess of acid is important. With constant stirring 10 ml. of the hydrogen peroxide are then run in from a pipette. The solution is allowed to stand for five minutes in a stoppered flask. The liberated iodine is then titrated in the ordinary way with standard (decinormal) sodium thiosulphate solution.

From the equation



and the relation



it should be evident that 2 litres of $\frac{N}{10}$ thiosulphate correspond to 3.4 gm.

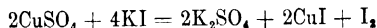
hydrogen peroxide. x ml. of $\frac{N}{10}$ thiosulphate is thus equivalent to

$\frac{3.4}{2000} \times \text{gm. of hydrogen peroxide.}$ The amount per litre (W gm.) is then

$\frac{3.4}{20} \times \text{gm.}$ The calculation from W of the volume strength is given on p. 73.

4. Estimation of Copper in a Specimen of Copper Sulphate.

Cupric salts react with potassium iodide to give a precipitate of cuprous iodide:



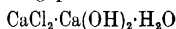
The presence of only a *little* free mineral acid does not affect the reaction, but it is desirable to neutralise the copper sulphate solution. In the presence of excess potassium iodide the change then takes place quantitatively. The copper sulphate solution should be about decinormal. From the equation one gram-equivalent of iodine is liberated by the formula weight in grams of the salt hydrate (249.7 gm.).

About 6 gm. of the powdered crystalline sulphate are weighed out and 250 ml. of solution made up. The solution is tested with litmus paper. If acid, each 25 ml. portion is treated with ammonium hydroxide, added drop by drop, until a slight permanent precipitate appears. This is then dissolved up with a little acetic acid. About 2 gm. of solid potassium iodide are then added, and the solution is stirred until this has dissolved. The solution goes dark brown with the liberated iodine. The titration

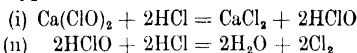
with decinormal sodium thiosulphate is then performed in the usual way, using starch indicator.

Note. The reappearance of the blue colour of starch iodide after the titration is apparently complete is a common source of difficulty in this titration. This is attributed to the effects of adsorption of iodine on the precipitated cuprous iodide. The use of a large excess of potassium iodide overcomes this difficulty. Alternatively about 0.5 gm. of solid ammonium thiocyanate may be added towards the end of the titration. This seems to have the effect of liberating the adsorbed iodine and enabling the titration to be completed with a sharp end point.

5. Estimation of Available Chlorine in Bleaching Powder. The chief constituents of bleaching powder are a basic chloride,

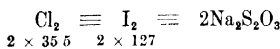


and calcium hypochlorite, Ca(ClO)_2 . When acidified the hypochlorite present liberates hypochlorous acid which breaks down :



It is this chlorine which is "available." The freshly made product may contain about 36 per cent. of its weight of available chlorine. The amount is conveniently determined by allowing the chlorine to displace iodine from potassium iodide, a method which is applicable to any hypochlorite.

About 5 gm. of the bleaching powder are accurately weighed out and rubbed to a thin paste with water in a large evaporating basin. The suspension is then transferred, with washings to a 500 ml. graduated flask and the volume made up with water. After mixing well, 50 ml. are taken in a pipette and transferred to a beaker-flask. 2 gm. of potassium iodide are added and then about 15 ml. of bench acetic acid. Acetic acid is preferred since sulphuric acid produces the sparingly soluble calcium sulphate, and hydrochloric acid, through being oxidised by any chlorate present, tends to cause high results. The titration of the iodine against standard sodium thiosulphate then follows the usual course. From the relationships :



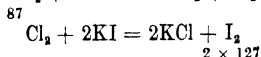
it will be clear that 1 litre of $\frac{\text{N}}{10}$ thiosulphate is equivalent to 3.55 gm. of chlorine.

6. Estimation of Manganese Dioxide in a Specimen of Pyrolusite.

Method I. Manganese dioxide is sometimes estimated by boiling it with concentrated hydrochloric acid and absorbing the chlorine evolved in excess potassium iodide solution. The changes which take place are :



and



About 0.5 gm. of the specimen is weighed out into the flask shown in Fig. 11, and about 100 ml. of concentrated hydrochloric acid are added. Each of the absorption tubes (large U-tubes) contains about 50 ml. of water and 3 gm. of potassium iodide. The apparatus is assembled with waxed corks and a small piece of magnesite is added to the contents of the flask before heating is commenced. The slow stream of carbon dioxide reduces the danger of iodide solution being sucked back at the end of the distillation. Distillation is continued until only about one-third of the original volume remains in the flask. The absorption tubes are then washed out with a little potassium iodide solution and the solution and washings are made up to 250 ml. in a graduated flask. Of this 50 ml. portions are titrated against standard sodium thiosulphate in the usual way, using starch solution as indicator.

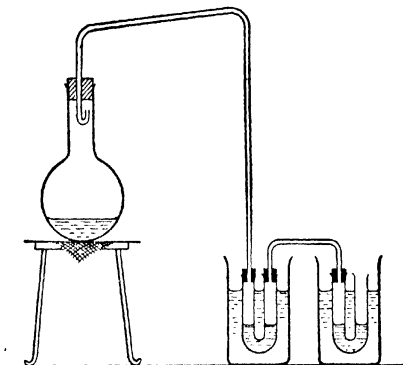
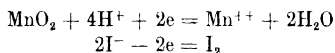


FIG. 11.

Method II. A procedure which has the merit of being simpler to carry out is to allow the powdered manganese dioxide to react with a mixture of hydrochloric acid and potassium iodide.



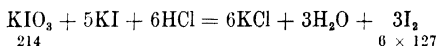
The latter change takes place under much weaker oxidising conditions than those required for the oxidation of chloride ion.

The experiment should be performed in duplicate. 0.2 gm. of the specimen of pyrolusite is accurately weighed out into a glass-stoppered flask of about 1 litre capacity. 2 gm. of potassium iodide are added, and then about 50 ml. of N hydrochloric acid. The flask is then closed and left to stand in the dark for quarter of an hour. At the end of this time, provided no black particles of the oxide are visible, the solution is diluted to about 500 ml. and standard thiosulphate solution is run in. Starch indicator is added when the solution becomes a straw colour.

The quantitative relations are the same as those for Method I, but different equations are required to represent the process of oxidation in this case. As is well known, manganese dioxide does not liberate chlorine from dilute hydrochloric acid in the cold. Mn_2O_3 as well as MnO_2 may be present, and the result will not show the specimen to be 100 per cent. MnO_2 . If ferric oxide is present in the specimen a more accurate result for MnO_2 will be obtained if N phosphoric acid is used in place of hydrochloric acid.

7. The Reaction between Iodic and Hydriodic Acids.

Potassium iodate is a chemical which can be obtained pure and can be made up in solution as a primary standard. By the reaction with excess potassium iodide in the presence of dilute acid:



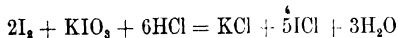
a standard solution of iodine can be obtained without any need of titration. Unfortunately an acid solution (containing hydriodic acid) changes in strength in the air owing to oxidation—a fact which should always be remembered when acid solutions containing iodine in potassium iodide are being used. It would have to be carefully neutralised if it were to be kept as a standard. The chief interest of the reaction is that it can be applied to obtain an independent check on the strength of a solution of hydrochloric or sulphuric acid—that is without the use of any other acid or alkali. A second reaction takes place in the presence of more concentrated acid (Experiment 2 below).

Experiment 1. Iodometric determination of hydrochloric or sulphuric acid in an approximately decinormal solution.

$\frac{N}{10}$ potassium iodate contains 3.566 gm. of the salt per litre. The solution can be made by weighing out the required amount. 25-ml. portions are treated with excess potassium iodide (about 1 gm.) and 25 ml. of the acid solution are run in from a pipette. Iodine is liberated quantitatively in accordance with the above equation. Using starch indicator, the iodine is titrated with standard sodium thiosulphate. It should be clear that 25 ml. of $\frac{N}{10}$ acid will liberate enough iodine to react with 25 ml. of $\frac{N}{10}$ thiosulphate.

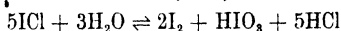
Experiment 2. Estimation of iodide ion concentration.

When a high concentration of hydrochloric acid is present and the potassium iodate is added in excess the iodine liberated in the reaction becomes converted to iodine monochloride:



Two molecules of iodine react in the formation of five molecules of iodine

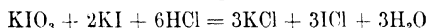
monochloride, the additional iodine coming from the iodate. To some extent the iodine monochloride is hydrolysed :



but this is much reduced by the presence of a high concentration of hydrogen ions. In these conditions the reaction between iodate and iodide can be applied to estimate iodide ion.

10 ml. of an iodide solution of about $\frac{N}{10}$ strength are placed in a glass-stoppered bottle of about 250 ml. capacity. 50 ml. of concentrated hydrochloric acid are added and then about 20 ml. of chloroform.* (The iodine present is largely taken up by the chloroform layer and the colour is readily perceptible.) On running in $\frac{N}{10}$ potassium iodate solution with frequent shaking, the chloroform layer first becomes red with liberated iodine and then, with more iodate, goes colourless. The point at which it becomes colourless is not sharply defined. The mean of at least three experiments should therefore be found.

By writing the change in one equation :

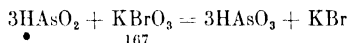


it becomes evident that 1 litre of M potassium iodate reacts with 2 litres of N potassium iodide. N potassium iodate is $\frac{M}{6}$ in molarity. Hence 10 ml. of $\frac{N}{10}$ potassium iodide require 30 ml. of $\frac{N}{10}$ iodate in this titration. The normality is therefore easily calculated.

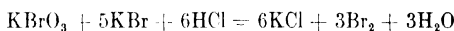
Other Oxidation-Reduction Titrations

Standardisation of a Solution of Sodium Arsenite with Potassium Bromate.

Potassium bromate of A.R. standard is readily obtainable and decinormal solution may therefore be made up by weighing out the required amount. With sodium arsenite in the presence of excess hydrochloric acid the bromate reacts according to the equation :



As soon as any excess bromate is added it reacts with the bromide to liberate bromine :



The bromine bleaches the methyl orange or methyl red added as an indicator. The disappearance of the red colour therefore marks the end point.

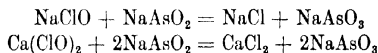
* Used chloroform should not be poured away. Using a separating funnel the chloroform layer may be quickly run off and poured into a bottle for chloroform residues. This may be distilled when a quantity has accumulated.

The equivalent of potassium bromate is one-sixth of the formula weight, viz. 27.82. 2.782 gm. are therefore needed to make 1 litre of decinormal solution. The salt is accurately weighed out and the solution made up in the usual way. The normality factor is calculated from the weight actually used. In doing a titration 25 ml. of a sodium arsenite solution, made up as described on p. 80, are strongly acidified by addition of concentrated hydrochloric acid and then a few drops of methyl orange are added. The bromate is run until the red colour just disappears.

This is a very good method of standardising arsenite solutions. The arsenite may be used to estimate the available chlorine in bleaching powder as described in the following exercise.

Estimation of Available Chlorine in Bleaching Powder by means of Sodium Arsenite Solution.

Sodium arsenite solution, standardised against potassium bromate (p. 85), or against iodine (p. 80) may be used to estimate hypochlorites:



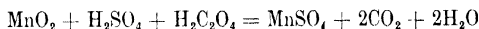
The end point of the titration is reached when a drop of the solution fails to produce a blue colour in starch iodide paper. This paper is prepared by soaking strips of filter paper in starch solution to which a little potassium iodide has been added. The test papers may be dried in the steam oven.

A suspension of bleaching powder is prepared as described on p. 82. 50 ml. of this are placed in a beaker-flask and standard sodium arsenite solution is run in from a burette. A drop of the mixture in the beaker-flask is tested on starch iodide paper at intervals until the end point is reached. Three results agreeing to within 0.1 ml. should be obtained.

Additional Exercises

1. Standardisation of Iodine against Sodium Arsenite. As an alternative to the procedure described on p. 79 a solution of iodine may be standardised by using pure resublimed arsenious oxide as a primary standard. The procedure for making up and using sodium arsenite is described on p. 80. This method of standardisation is in many ways to be preferred to the use of thiosulphate.

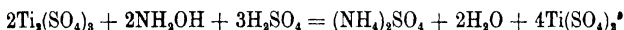
2. Determination of Manganese Dioxide by oxidation of Oxalic Acid. About 0.4 gm. of the finely powdered oxide is heated with 50 ml. $\frac{\text{N}}{5}$ oxalic acid and 20 ml. bench sulphuric acid on the water bath until no black particles are visible.



The solution is then diluted with about 200 ml. of hot water and titrated while hot with decinormal potassium permanganate. In this way the

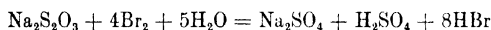
excess oxalic acid is estimated and the amount of dioxide in the specimen can be calculated. The experiment should be performed in duplicate.

3. Determination of Hydroxylamine in a Solution by titration with standard Titanous Sulphate. Titanous sulphate reduces hydroxylamine quantitatively to ammonia. In acid solution the change is then as shown :



25 ml. portions of the given solution of hydroxylamine sulphate (5 or 6 gm. per litre) or hydroxylamine hydrochloride (3 or 4 gm. per litre) are titrated direct against decinormal titanous sulphate solution. The latter should have been recently standardised. The indicator is methylene blue, the colour of which is just discharged at the end point. More accurate results are obtained if the titration is carried out after warming the hydroxylamine sulphate solution to 30° or 40° C.

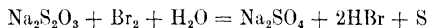
4. The reaction between Sodium Thiosulphate and Bromine Water. This reaction is said to follow the course indicated by the equation :



This may be verified by a simple experiment. In addition to ordinary bromine water (made by shaking some distilled water with a little bromine in excess), $\frac{\text{M}}{10}$ sodium thiosulphate and $\frac{\text{M}}{10}$ potassium iodide solutions are required. Starch solution and some starch iodide paper are needed as indicators.

It is first necessary to find the molarity of the bromine solution. 25 ml. of this are run from a *burette* into 50 ml. of the $\frac{\text{M}}{10}$ potassium iodide solution. The iodine liberated is then titrated with standard thiosulphate solution, using starch solution as indicator.

50 ml. of the bromine solution are then run into a conical flask from a *burette*. Standard thiosulphate is then run in very slowly with frequent shaking. A precipitate of sulphur forms transiently owing to the reaction



but this disappears owing to further oxidation to sulphuric acid. When the colour of the bromine is almost gone the titration is continued with the use of starch iodide paper as external indicator. The blue colour indicates the presence of bromine. It will be seen that from the equation for the complete reaction, 50 ml. of $\frac{\text{M}}{10}$ bromine solution will react with 12.5 ml. of $\frac{\text{M}}{10}$ thiosulphate solution. Chlorine water reacts in an exactly similar way, oxidising the thiosulphate to sulphate.

PRECIPITATION PROCESSES

The discussion of solubility product given in the Introduction (p. 8) is not satisfactory, since it is now certain that practically all salts are ionised in the solid state and are completely dissociated in solution. A treatment which is more in accordance with modern ideas has been suggested by Butler (1924). This treatment does not postulate the existence of molecules of salts but only their ions.

A crystal of an ionised solid is a lattice of ions and the surface of such a solid is a regular mozaic of $+$ and $-$ ions. Whatever the mechanism by which an ion is detached from the crystal lattice, the rate of leaving the surface must be proportional to the number of that kind of ion per unit area at that instant. In the second place, the rate at which one kind of ion is deposited from solution must be proportional to (a) the concentration of that kind of ion in solution, and (b) the number of places at which these ions can be accommodated so as to continue the crystal lattice. Removal of a $+$ ion from the surface layer of a lattice of the type shown will expose the $-$ ion



underneath, and vice versa. At equilibrium (in contact with a solution saturated with respect to both kinds of ion) the rates of solution and deposition will be equal for both kinds of ion, so that equal numbers leave and arrive in each case.

If there are Nx $+$ ve ions and $N(1-x)$ $-$ ve ions per unit area at equilibrium the rates of solution for the two types will be given by

$$\begin{array}{ll} +\text{ve ions :} & k_1Nx \\ -\text{ve ions :} & k_2N(1-x) \end{array}$$

On the other hand the rates of deposition will be given by

$$\begin{array}{ll} +\text{ve ions :} & k_3N(1-x)[B^+] \\ -\text{ve ions :} & k_4Nx[A^-] \end{array}$$

where $[B^+]$ and $[A^-]$ are the concentrations in gram-ions per litre of the two ions at equilibrium. For equilibrium in the two processes for each ion :

$$\begin{aligned} k_1Nx &= k_3N(1-x)[B^+] \\ k_2N(1-x) &= k_4Nx[A^-] \end{aligned}$$

whence

$$\begin{aligned} [B^+][A^-] &= \frac{k_1Nx}{k_3N(1-x)} \cdot \frac{k_2N(1-x)}{k_4Nx} \\ &= \frac{k_1k_2}{k_3k_4} = \text{constant (S)}. \end{aligned}$$

Applying this to silver chloride solution in contact with the solid :

$$[\text{Ag}^+][\text{Cl}^-] = S$$

where S is the solubility product. The value of S at 18° is found to be 1.1×10^{-10} . This means that in the presence of a slight excess of chloride ion all the silver ion in a solution will be precipitated with the exception of the amount required to maintain the solubility product at this (extremely small) value. Alternatively a slight excess of silver ion may be added, and the chloride ion concentration will then be reduced to a similar low value given by

$$[\text{Cl}^-] = \frac{S}{[\text{Ag}^+]}$$

It is clearly impossible to precipitate *all* the chloride ion and the form of the graph obtained by plotting $[\text{Cl}^-]$ against $[\text{Ag}^+]$ is of hyperbolic form (Fig. 12). In practice a very moderate excess of silver ion will suffice to

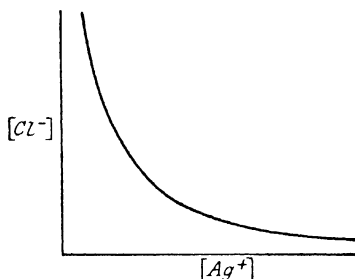


FIG. 12.

reduce the chloride ion concentration to a negligibly small value. A large excess of silver ion is undesirable since there is always a tendency for ions to be adsorbed on the surface of a precipitate. This leads to errors whether the precipitate is weighed or whether the excess silver ion is afterwards determined by titration. This precaution is observed as a general rule in precipitation processes, there is the further danger that in some cases a large excess of reagent will lead to secondary reactions with the precipitate, e.g. in the formation of complex ions.

We come now to the problem of how to determine the end-point (or equivalence point) of a titration which is accompanied by the formation of a precipitate. In the absence of a good method there will be no alternative to a gravimetric method: the precipitate when formed under optimum conditions must be filtered off, washed, dried and weighed. When possible, however, much time may be saved by using a volumetric method in which a definite end point or equivalence point is given. These are obtained in one of two ways (excluding conductometric methods):

(i) *Coloured salt formation*: an ion is introduced into the reaction mixture which will form a coloured product *after* the main reaction is over. Thus potassium chromate is sometimes used as an indicator in the titration of silver nitrate against chloride in neutral solution (Mohr's method, p. 91). As soon as a slight excess of silver ion is present some red silver chromate is formed. The solubility products are:

$$[\text{Ag}^+][\text{Cl}^-] = 1.1 \times 10^{-10} \quad (\text{i})$$

$$[\text{Ag}^+]^2 [\text{CrO}_4^{--}] = 2 \times 10^{-12}$$

whence

$$[\text{Ag}^+][\text{CrO}_4^{--}]^{\frac{1}{2}} = 1.414 \times 10^{-6} \quad (\text{ii})$$

The values given in (i) and (ii) are the ones to compare. It will be clear that so long as there is any appreciable concentration of Cl^- ion it will appropriate the silver ions to such an extent that the solubility product of silver chromate is not reached.* With the usual amount of chromate ion present the red colour of silver chromate is not seen until the chloride is practically entirely removed.

(ii) *Adsorption indicators*. An important contribution to analytical methods has been made by the discovery by Fajans, Kolthoff and others that certain dyes can be used as adsorption indicators. Precipitates such as the silver halides are at least partly in a colloidal state when they are first formed. The ions of certain dyes are adsorbed on the surface of these colloidal particles. The interesting point about this is that in general the anions of dyes are more strongly adsorbed on the precipitate in the presence of a slight excess of the positive ion (cation) present in the precipitate. When fluorescein, for example, is present during a titration of potassium chloride against silver nitrate (the latter being in the burette), up to the equivalence point the solution has the ordinary greenish-yellow fluorescence. Immediately an excess of silver ions is present the precipitate becomes a bright pink in colour. This is because fluorescein anions have become strongly adsorbed on the silver chloride.

Fluorescein may be used in the form of its sodium salt (soluble in water) or dissolved in alcohol. In either case, when a little of the solution is added to the titration mixture, there are sufficient of the anions present. Practical details are given later.

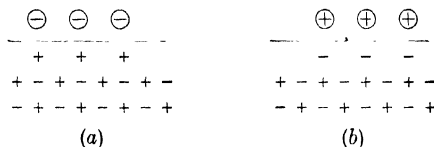
There are certain basic dyes which are strongly adsorbed in the presence of an excess of the negative ion. In this case it is the cations of the dye which are adsorbed. The figure represents the two different cases:

- (a) the surface of a colloidal particle which is positively charged and
- (b) the surface of a colloidal particle which is negatively charged.

* The point may be made clearer by noting that the first formation of silver chromate will occur at a point when the silver ion concentration is such that there is equilibrium with both precipitates. Otherwise the more soluble silver salt will be used up to form more of the less soluble one.

$$\begin{aligned}
 [\text{Ag}^+] &= \frac{1.1 \times 10^{-10}}{[\text{Cl}^-]} \\
 &= \sqrt{\frac{2 \times 10^{-12}}{[\text{CrO}_4^{--}]}}
 \end{aligned}$$

The lower layers of ions represent the interior of the crystal; the charges marked with a circle represent the ions of the dye adsorbed on the surface.



The exercises selected for this book are limited to the use of silver nitrate. The principles of precipitation processes can be learnt very conveniently in the use of this reagent.

Preparation of Standard Silver Nitrate Solution.

Silver nitrate of A.R. standard (or recrystallised from dilute nitric acid, washed and dried) may be weighed out as a primary standard. The equivalent of the salt is 169.88. 8.494 gm. are therefore needed to make 500 ml. of decinormal solution.

The pure silver nitrate should be dried in an air oven for at least an hour and then kept in a desiccator. About 8.5 gm. are then accurately weighed out from a weighing bottle into a clean beaker. Distilled water is added, and the solution, total volume 500 ml., is made up in the usual way. It is advisable to test the distilled water for chloride beforehand. The normality may be calculated from the weight of silver nitrate used.

Titration of Silver Nitrate with Sodium Halide.*

Silver nitrate solution is sometimes made up to be only approximately decinormal. It can then be standardised against a standard solution of sodium chloride since the latter salt can be obtained in great purity and used as a primary standard. For 1 litre of decinormal sodium chloride 5.85 gm. are needed. Alternatively the same procedure is followed to standardise chloride solution when standard silver nitrate is available.

It is assumed here that it is the chloride solution which is of unknown strength. If the solution is *neutral* either Mohr's method or Fajans's method may be used. For acid solutions Volhard's method must be used for reasons given below.

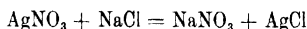
Method I. Mohr's method.

Potassium chromate is used as an indicator. The theory of the titration has been indicated on p. 90.

25 ml. of the neutral and approximately decinormal chloride are taken in a pipette and placed in a conical flask or beaker-flask. About 1 ml. of 5 per cent. potassium chromate solution is added and then standard silver nitrate is run in from the burette. A white precipitate is formed, accompanied in the later stages by a transient red coloration. The end point

* The methods described here can, of course, be applied under the appropriate conditions to the titration of any chloride in solution.

is marked by the appearance of a permanent reddish-brown coloration, due to silver chromate. One approximate and three accurate titrations should be carried out. A little practice is required to judge the end point. The waste mixture in the titration vessel should be poured into a bottle for silver residues.



The normality of the chloride solution is calculated from the result.

Note.

(i) Mohr's method can be used to estimate bromides, but not iodides in neutral solution.

(ii) After taking 25 ml. of the chloride solution it may be made neutral if it is either acid or alkaline. Acid solutions are treated with a little calcium carbonate (slight excess), alkaline solutions are neutralised with dilute nitric acid, using litmus paper.

(iii) Potassium dichromate cannot be used in place of potassium chromate because silver dichromate is much more soluble than the chromate, and too large an excess of silver ion is therefore required.

Method II. Fajans's method.

The adsorption indicator which is used here is made by dissolving 0.2 gm. of fluorescein in 100 ml. of alcohol. Alternatively 0.2 gm. of the sodium salt of fluorescein is dissolved in 100 ml. of water. Other indicators are also in general use. The theory of the method has been indreated on p. 90.

25 ml. of the approximately decinormal chloride solution are placed in a bottle of about 150 ml. capacity fitted with a ground glass stopper. Six drops only of the indicator are added, and then standard silver nitrate is run in from the burette, the bottle being shaken vigorously at intervals. Before the end point is reached the mixture is yellow, and each addition of silver nitrate produces a local reddish-violet coloration. Just before the end point the precipitate coagulates and at the end point becomes itself a reddish-violet colour.

Note.

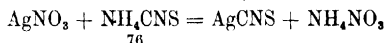
(i) If bromide or iodide is estimated instead of chloride, eosin (tetra-brom-fluorescein) solution should be used as indicator (it is made up in the same way) and the end point is similar. Eosin is not suitable for chlorides, however, since it is found to be adsorbed and thus colours the precipitate before the end point is reached.

(ii) Fajans's method requires cold neutral solutions. Calcium, barium and strontium salts, and other multivalent cations should not be present, since these exert a powerful coagulating effect on the silver halide sol.

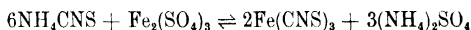
(iii) Practice in noting the end point with these indicators may usefully be obtained by first using solutions previously titrated by Mohr's method or Volhard's method.

Method III. Volhard's method.

In acid conditions potassium chromate cannot be used as an indicator for silver nitrate titrations because silver chromate is soluble in acid. The accuracy of Mohr's method in any case is not very high and, moreover, it is not a good method for estimating iodides. Volhard's method calls for the use of a second reagent: potassium or ammonium thiocyanate, which reacts with silver nitrate, as shown:



The method consists, then, of treating a measured volume of the halide solution with a known volume of standard silver nitrate which is somewhat in excess of that required to react with the halide. The titration of the excess silver nitrate is then performed, using standard ammonium thiocyanate and a little ferric salt as an indicator. The behaviour of the indicator is reversible:



Consequently a transient red colour is seen during the titration, and at the end point the red colour of ferric thiocyanate becomes permanent. An important note on this end point is given below (p. 94).

Standardisation of Ammonium Thiocyanate. About 7.5 gm. of ammonium thiocyanate (or 10 gm. of the potassium salt) are weighed out and dissolved in water to make 1 litre of solution. Both of these salts being deliquescent, they are unsuitable as primary standards. The solution is therefore standardised against standard silver nitrate. 25 ml. of the latter are placed in a beaker-flask and 1 or 2 ml. of saturated iron alum solution (acidified with nitric acid) added. The same quantity of indicator solution should be used in each titration to obtain consistent results. On running the thiocyanate solution in from the burette a white precipitate of silver thiocyanate is formed, and at the end point the red colour of ferric thiocyanate becomes permanent. The normality of the thiocyanate is then calculated.

Procedure for determining halide. 25 ml. of the halide solution (approximately $\frac{N}{10}$) are placed in a beaker-flask and treated with 50 ml. of standard (decinormal) silver nitrate. 1 or 2 ml. of the iron alum indicator is then added and, with frequent stirring, standard ammonium (or potassium) thiocyanate is run in from the burette. The end point is marked by the appearance of a permanent red coloration. As noted above, the same quantity of indicator should be used in successive titrations.

Supposing that the silver nitrate is 0.09 N and in the titration x ml. of 0.1 N NH_4CNS are used, the normality of the halide is found as follows:

$$x \text{ ml. } 0.1 \text{ N } \text{NH}_4\text{CNS} = \frac{0.1}{0.09} x \text{ ml. of } 0.09 \text{ N } \text{AgNO}_3$$

$$\therefore 25 \text{ ml. of halide} = \left(50 - \frac{0.1}{0.09} x\right) \text{ ml. of } 0.09 \text{ N } \text{AgNO}_3$$

from which the normality is obtained.

Note on the End-point of this Titration. A more accurate result may be obtained, when estimating *chloride*, by filtering the solution before doing the titration with thiocyanate. The precipitate of silver chloride must be thoroughly washed with water on the filter and the filtrate and washings are then titrated with standard thiocyanate, using iron alum indicator.

When estimating bromide or iodide the titration can be done in the presence of the precipitated silver halide, and there is no need to filter. The reason for this lies in the solubility products of the respective silver salts :

$[\text{Ag}^+][\text{Cl}^-]$	1.2×10^{-10}
$[\text{Ag}^+][\text{CNS}^-]$	1.0×10^{-12}
$[\text{Ag}^+][\text{Br}^-]$	3.5×10^{-13}
$[\text{Ag}^+][\text{I}^-]$	1.0×10^{-16}

Owing to its lower solubility silver thiocyanate is formed when silver chloride is in contact with thiocyanate ions :

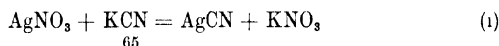


This means that there is a tendency for the red colour of ferric thiocyanate not to develop until there is a considerable excess of ammonium thiocyanate present. This difficulty does not arise in the case of the other silver halides.

Determination of Iodide. The precipitation of silver iodide is nearly always attended by the "carrying down" of either the iodide or of silver nitrate. This means that the precipitate is contaminated with one or other of these substances. This source of error is minimised by using dilute solutions and by shaking vigorously in a stoppered bottle after the addition of each 2 or 3 ml. of silver nitrate.

Determination of Cyanide in a Solution by Titration with Standard Silver Nitrate.

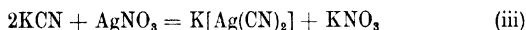
When silver nitrate solution is added to a solution of a cyanide the silver cyanide formed is not precipitated so long as excess of cyanide is present. This is because the reaction



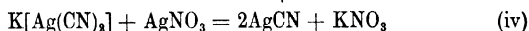
is followed by the formation of the soluble potassium argentocyanide :



Adding (i) and (ii) we obtain :



When more silver nitrate is run in a point is reached when the complex salt reacts according to the equation :



The point at which this change begins to occur is marked by the first

appearance of turbidity. This accordingly marks the end of the change shown in equation (iii). The solubility product of AgCN is 2×10^{-12} .

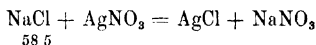
Procedure. An ordinary pipette is NEVER used to measure out portions of the approximately decinormal cyanide solution. This is because of its excessively poisonous nature and because of the vapour of hydrocyanic acid present owing to hydrolysis. In place of a pipette a second burette may conveniently be used. 25 ml. are measured out from this and immediately titrated with standard silver nitrate to the point of appearance of a faint permanent turbidity. The volume of silver nitrate used will be seen from equation (iii) to be exactly half that required for complete double decomposition according to equation (i). If, therefore, x ml. of decinormal silver nitrate are used in the titration, $2x$ ml. are required for equivalence according to equation (i), and it is on this basis that the normality must be calculated.

Additional Exercises

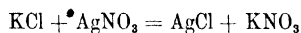
1. The Determination of the Equivalent of a metal given a soluble chloride (or other halide). The equivalent of a metal combines with 35.5 parts by weight of chlorine. Provided the halide is anhydrous or, as in the case of barium chloride, can be ignited carefully without hydrolysis so that the percentage of water of crystallisation is known, the equivalent of a metal can be found by titration. It is simply necessary to make up a solution containing a known weight of the salt or its hydrate in one litre and then titrate this with standard silver nitrate, preferably by Fajans's or Volhard's method. If there is any tendency towards hydrolysis in aqueous solution a little nitric acid (free from halide) may be added, provided Volhard's procedure is then followed.

The calculation follows simply from the determination of the normality of the solution with respect to halogen ion. An x Normal solution of chloride ion will, of course, be x Normal with respect to the metal.

2. The Determination of two halides present in a solution. If the solution contains a known weight of the mixed salts per litre and the identity of the salts is not in doubt, the composition of the mixture is determined by a simple titration against standard silver nitrate. A mixture of sodium and potassium chlorides may be considered in illustration. If the weight of solid is m gm. per litre and the solution proves to be $y \times \frac{N}{10}$ with respect to chloride ion we may put the concentration of one of the chlorides equal to x gm. per litre and the other to $m - x$ gm. per litre. From the equations:



58.5



74.5

it is clear that 5.85 gm. of sodium chloride require one litre of decinormal

silver nitrate, and 7.45 gm. of potassium chloride likewise require one litre. It follows that x gm. of sodium chloride require $\frac{x}{5.85}$ litres of decinormal silver nitrate and $(m - x)$ gm. of potassium chloride require $\frac{m - x}{7.45}$ litres of decinormal silver nitrate. But, from actual titration 1 litre of the halide requires y litres of decinormal silver nitrate. We have then :

$$\frac{x}{5.85} + \frac{m - x}{7.45} = y$$

and both m and y are known.

This method can obviously be applied to the determination of mixtures of two halides of the same metal as, for example, potassium chloride and bromide. Its accuracy depends, however, on the amount of the difference between the equivalents of the two salts and the results are not good when this difference is small.

3. Estimation of chloride and acid in a solution containing both.

The solution should be approximately decinormal with respect to both chloride and hydrogen ion (e.g. HCl and NaCl). The presence of chloride ion does not hinder the titration of the acid present against standard alkali. 25 ml. of the solution are titrated with standard $\left(\frac{N}{10}\right)$ caustic soda, using methyl red or litmus indicator.

The determination of chloride ion must be carried out by Volhard's method (p. 93). 25 ml. of the solution are treated with 50 ml. of decinormal silver nitrate. The excess silver nitrate is then titrated against standard ammonium thiocyanate (iron alum solution indicator).

4. Estimation of chloride and alkali in a solution containing both.

The solution should be approximately decinormal with respect to both chloride and hydroxyl ion (e.g. NaOH and NaCl). The simplest procedure is to neutralise the alkali with standard hydrochloric acid and then titrate the *total* chloride ion in the resulting neutral solution against standard silver nitrate (Mohr's method).

25 ml. of the solution are first neutralised, using decinormal hydrochloric acid using phenolphthalein indicator. When the colour of the indicator is just discharged decinormal silver nitrate is run in from a burette. Potassium chromate solution is used as indicator.

If x ml. of $\frac{N}{10}$ hydrochloric acid are used, and y ml. of $\frac{N}{10}$ silver nitrate, it follows that $(y - x)$ ml. of the silver nitrate have been used in reacting with the chloride ion originally present in 25 ml. of the mixed solution.

GRAVIMETRIC ANALYSIS

Gravimetric analysis consists of isolating and weighing an element or a definite compound obtained from a substance and from the weight inferring the composition of the substance analysed. Just as in volumetric analysis, each analysis gives information concerning the amount of one particular constituent. *Complete* analysis of a substance usually entails a series of analyses unless the substance is relatively simple and comparatively pure. The exercises given here are limited to the determination of one or two metals and acid radicals—enough merely to introduce the student to the fundamental principles.

Precipitation.

When we desire to estimate an element or compound by weighing it as a solid precipitate, it is clearly essential to ensure complete precipitation and, what is just as important, to obtain the precipitate in the form of a compound of definite composition which can be either ignited or dried to constant weight.

To secure the first of these desiderata we must consult tables of solubility products and limit ourselves to substances which have extremely low solubilities at room temperature. Moreover, precipitation must be carried out under conditions which, so far as possible, minimise loss due even to the low solubility. It is an interesting point that, in spite of the greater solubility at higher temperatures, it is usually preferable to carry out a precipitation at or near the boiling point of a solution and then to allow the mixture to cool after a period of boiling. Careful investigation has shown that calcium, barium and strontium sulphates, for example, are much more soluble when in a finely divided condition. Thus, Hulett showed that saturated gypsum solution at 25° C. contained 2.080 gm. per litre. On shaking the solution with very finely divided gypsum the solubility was increased to 2.542 gm. per litre. Similar results have been recorded for many other sparingly soluble substances, but it cannot be said that the phenomenon is as yet very well explained. The facts are that many precipitates, when first formed, are partly colloidal and consequently are more soluble and filter badly. On boiling the smaller particles cohere and form larger ones, which are less soluble and much more easily separated by filtration.

Besides the formation of colloidal or finely divided precipitates the other bugbear of gravimetric work is the "carrying down" of other substances along with the required precipitate. Kolthoff has shown that more than one cause may account for this trouble. The tendency has been to use the terms adsorption and occlusion rather loosely in this connexion. Occlusion should refer to the retention of "impurities"—including water—*inside* the crystalline particles. Ordinary *surface* adsorption accounts for the retention of substances on the precipitate after it has

been formed. There are, besides, effects due to the formation of solid solutions ("mixed crystals") and compound formation, but these are more rare.

It may be objected that such sources of error are not of great moment in discussing exercises suitable for the beginner. It is, however, necessary from the beginning to appreciate the need of carefully regulated conditions for the formation of precipitates. The conditions of concentration, hydrogen ion concentration and temperature must be properly controlled and the directions given below exactly followed.

Filtration.

A precipitate which is suitable for separation will, in most cases, form a fairly compact deposit at the bottom of the beaker. Filtration is then carried out expeditiously by first decanting the supernatant solution into

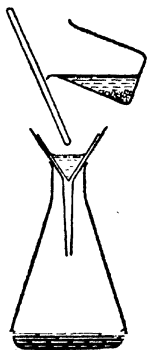


FIG. 13.

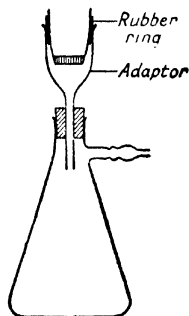


FIG. 14.

the filter. When most of this solution has run through the filter the precipitate can be transferred with as few operations as possible. The last traces must be washed from the sides of the beaker with the jet from the wash bottle. A "policeman" is useful for loosening the last traces of solid from the glass so that it can be washed into the filter. Washing on the filter is usually done to the point when the filtrate gives no reaction to a suitable test for ions.

A precipitate is filtered off for weighing on either "ashless" filter paper or on some kind of Gooch crucible. There are several grades of "ashless" filter paper, which differ in the coarseness of the filtering medium. A finer paper is required for barium sulphate than for ferric hydroxide, for example. On each packet the manufacturer gives the (average) weight of ash left on burning one paper. Papers carrying precipitates are always first dried in the oven and then carefully burnt over a tared crucible. Filtration on paper is accordingly not desirable if the

precipitate is readily reduced by contact with hot carbon. To burn the paper it may be folded carefully, so that no solid can be lost, and held in the tongs over the crucible until about half is burnt away. The remainder will go into the crucible without projecting over the edge.

In selecting a paper of suitable diameter it must be remembered that on no account must the folded paper project beyond the edge of the funnel. Also the paper is not filled completely; a clean strip about 2 cm. wide should be seen after the filtration is completed.

A Gooch crucible, fitted with an adaptor in the neck of a filter flask, is shown in Fig. 14. Two types are in common use: (a) a crucible with a perforated bottom, requiring a mat of pulped asbestos as the filter medium, and (b) a Jena glass crucible with a bottom of sintered glass of a selected grade of porosity. The former are made of porcelain and can be heated strongly; the latter are not suited to the ignition of a precipitate, and are used only when the precipitate is to be dried in the oven to constant weight.*

In the preparation of the first type of Gooch crucible some asbestos fibre which has been freed from all soluble matter is stirred with distilled water and poured into the crucible without applying suction. When a mat has formed at the bottom about 100 ml. of distilled water are passed through with gentle suction from the filter pump. A thin compact mat about 2 or 3 mm. thick is required. The crucible is finally dried to constant weight in an oven at the temperature which will be required for the precipitate. It must be allowed to cool in a desiccator before weighing.

Sintered glass crucibles cannot be heated above about 500° C. Apart from this limitation they are very useful, since no preparation is necessary beyond drying in the oven. They may be cleaned by immersion in strong nitric acid, or chromic acid or any other suitable reagent having regard to the nature of the residue in the crucible. They are then washed with distilled water and dried to constant weight.

Using the first type of Gooch crucible it is important to filter only with suction applied, and to disconnect the suction before turning off the water tap. Neglect of this precaution may cause the filtered solid and the asbestos mat to become detached from the crucible bottom, and may cause a break in the filter medium.

Determination of Sulphate Radical in a soluble Sulphate.†

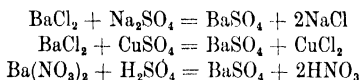
Barium sulphate has a solubility product of 10^{-10} at room temperature. This is a solubility of about 0.0002 gm. in 100 ml. of water. The solubility is of the same order as that of silver chloride. The substance is therefore a suitable one for gravimetric estimation of either barium or sulphate, provided that it is precipitated under carefully regulated conditions. A little hydrochloric acid should be present to prevent precipitation of sulphite or carbonate, but in Normal hydrochloric acid the

* A recent development, however, is the *Vitreosil* filtering and ignition crucible which can be heated to 1000° C.

† Alternatively of Barium in a soluble salt.

solubility of barium sulphate is three times as great as in water, so a large excess of acid must be avoided. The "carrying down" of other substances by barium sulphate is marked, so the precipitation is done by slow addition of the barium salt solution to the boiling sulphate solution.

Since it is desirable to have about 0.5 to 1.0 gm. of precipitate to weigh at the end, the weight of sulphate or of barium salt to be used should be calculated. In the examples:



convenient weights would be: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 0.7 gm.; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.5 gm.; $\text{Ba}(\text{NO}_3)_2$ 0.5 gm.

Assuming that sulphate is to be determined the requisite amount is weighed out twice, and the two samples are dissolved separately in about 150 ml. of water in beakers of about 350 ml. capacity. The procedure is carried out in duplicate throughout, the beakers being labelled A and B to avoid mistakes. About 5 ml. of dilute hydrochloric acid are added and the beakers placed over a flame or on a hot plate. When the solution is boiling gently, barium chloride solution is added very slowly. This solution should be about 0.25 M (61 gm. of the salt in one litre), and about 20 ml. should be added. The beakers are then placed on the bench and the mixtures allowed to settle. The addition of a drop of barium chloride to the clear supernatant solution will then show if the precipitation has been completed. If not, a further 5 ml. are added and then a further test is made. The mixtures are then kept hot but not boiling for about an hour, watch glasses being placed on as covers against dust. It is as well to rinse the under side of the glasses when removing them, using for this purpose the jet of the wash bottle. During this interval for digesting the precipitate, porcelain Gooch crucibles may be prepared in the manner described on p. 99. These must be dried over a strong Bunsen flame and allowed to cool in a desiccator. After a second short heating the weight should remain unchanged.

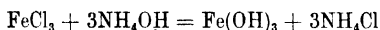
While still warm the clear solution is carefully poured by decantation through the Gooch crucible, using suction. After transferring the precipitate in the manner described on p. 98, it must be washed on the filter with distilled water until the filtrate shows no turbidity with silver nitrate solution. The Gooch crucible is then heated over a flame, gently at first and finally to dull redness for about ten minutes. The crucible is allowed to cool in a desiccator and then weighed. It should be heated again and reweighed when cool, this process being continued until the weight is constant. It should not be necessary to weigh more than twice the weights can be left on the balance pan in the interval. From the weight of barium sulphate obtained it is simple to calculate the weight of sulphate radical in the original specimen, and thus the percentage of sulphate.

Note. The determination of barium in a soluble barium salt is per-

formed in a closely similar manner. Samples of about 0.5 gm. are accurately weighed out, dissolved in water, and the precipitation carried out by the addition of dilute sulphuric acid to the boiling solution.

Determination of Iron in a Sample of Iron Oxide

Iron oxide, whether Fe_2O_3 or Fe_3O_4 , dissolves satisfactorily only in fairly concentrated hydrochloric acid. A little nitric acid is then added to oxidise any ferrous salt to the ferric state. By the addition of ammonium hydroxide a gelatinous precipitate of ferric hydroxide is obtained.



This is converted to the oxide Fe_2O_3 by igniting at red heat. Other heavy metals must be absent.

The points of procedure worthy of note are :

- (i) the washing of the precipitate by decantation before transferring the bulk to filter ;
- (ii) washing with 1 per cent. ammonium nitrate solution to coagulate colloid ;
- (iii) the precipitate is bulky, and when compressed is not readily penetrated by water. For this reason a filter paper is preferred to a Gooch crucible ;
- (iv) ignition of the paper must be carried out with access of the air to avoid reduction of iron oxide by carbon.

Two 0.5 gm. samples are accurately weighed out into 150 ml. beakers and dissolved in about 20 ml. of concentrated hydrochloric acid and 10 ml. of water. The action is slow and requires gentle heat for about half an hour. More acid and water may be needed to replace that evaporated. About 1 ml. of concentrated nitric acid is then added to the solution, which is boiled and then diluted to about 60 or 70 ml. before filtering into a clean beaker of about 350 ml. capacity. The filter should be washed well with weak hydrochloric acid.

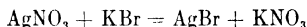
Before making the solution alkaline it is diluted to about 200 ml. and brought to the boiling point. Strong ammonia solution is then added slowly and with constant stirring until the mixture smells of ammonia. The ferric hydroxide coagulates and should form a layer at the bottom of the vessel after a further minute's boiling. The clear and colourless supernatant liquid is then decanted through a filter. The precipitate is then washed by decantation several times, using for this purpose a hot 1 per cent. solution of ammonium nitrate. The precipitate is finally transferred to the filter, washed with more ammonium nitrate until free from chloride, and then the filter paper and contents are dried and ignited in an open crucible, which was previously ignited and weighed. The paper and precipitate are first dried over a low flame and then heated to redness for half an hour. Ignition should be carried out to constant weight.

Determination of Halide (or alternatively Silver) in a soluble salt.

Silver chloride is only very slightly soluble—about 0.0017 gm. per litre at 20° C. The chief difficulty attending its manipulation is that it tends to become colloidal and pass through the filter. The presence of nitric acid largely prevents this. By precipitating and weighing silver halide, it is clear, either halide or silver can be estimated. It is assumed here that halide is to be estimated.

0.5 gm. of the specimen of the chloride, bromide or iodide is accurately weighed out and dissolved in about 100 ml. of water. The solution is acidified with dilute nitric acid and heated to boiling point. About 20 ml. of silver nitrate (about 0.5 N) are then added slowly with constant stirring. The precipitate is then allowed to settle, and one or two drops of silver nitrate are added to the clear supernatant solution. This shows if precipitation has been complete.

E.g.

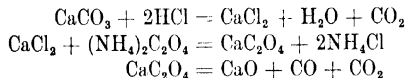


Filtration of the silver halide from the hot solution is best effected on a sintered glass filter crucible, but if this is not available an ordinary Gooch crucible should be prepared. In either case the crucible is dried in the air oven at about 150° C. to constant weight. The clear solution is first decanted through the filter, and then the precipitate is washed by decantation with a little cold and *very* dilute nitric acid. When it has been transferred to the filter the precipitate is again washed with the very dilute acid until the filtrate is free from silver ion. The filter crucible is then dried to constant weight at about 150° C. in the air oven. “

Since silver halides are sensitive to light the precipitate must be placed in a cupboard if the analysis is interrupted. It should be evident how the procedure may be modified if silver instead of halide is to be determined. The solution of the nitrate is then treated with dilute hydrochloric acid and the subsequent procedure for dealing with the precipitate is as above. All silver salts which are soluble in nitric acid can be determined in this way.

Additional Exercises**1. Determination of Calcium Oxide in Calcium Carbonate.**

Precipitation of the metal as calcium oxalate from a solution of the chloride is suitable provided heavy metals are not present. On ignition the oxalate is converted into the oxide

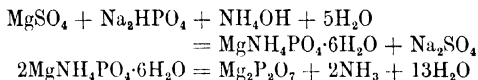


0.5 gm. samples of the carbonate are weighed out into large (400 ml.) beakers. 20 or 30 ml. of water are added and then sufficient dilute hydrochloric acid to dissolve the solid on warming. The beakers should be covered with watch glasses during the effervescence. The solution is

then diluted to about 100 ml. with water and heated nearly to boiling. A moderate excess of ammonium oxalate solution is then added (there should be about 1 gm. of ammonium oxalate present), and this is followed by sufficient ammonium hydroxide to make the solution alkaline. After standing for at least an hour the precipitate is separated by filtration on a prepared Gooch crucible, which has been dried at dull red heat to constant weight. The precipitate must be washed with water until the last few drops passing through give no turbidity with silver nitrate. The Gooch and its contents are then dried in the steam oven, and finally ignited almost to dull redness for about quarter of an hour.

2. Determination of Magnesium in Magnesium Sulphate.

Precipitation of the metal as magnesium ammonium orthophosphate is suitable provided heavy metals are not also present. Ignition of the precipitate yields the pyrophosphate:



0.5 gm. samples of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, are weighed out into 250 ml. beakers and dissolved in about 50 ml. of water. About 25 ml. of bench ammonium chloride are then added, followed by about 30 to 40 ml. of bench ammonium hydroxide. If any precipitate is formed at this stage it is redissolved by addition of more ammonium chloride. To the clear alkaline solution an excess of sodium phosphate solution is now added. A glass rod tipped with rubber should be used for stirring, and it should not be allowed to touch the sides of the beaker as there is a tendency for the precipitate to adhere to the sides. The supernatant solution is then decanted through a prepared Gooch crucible (ignited at redness to constant weight), and then it is washed with a little cold weak ammonium hydroxide until the filtrate is free from all trace of chloride. As little washing as possible should be done. The Gooch crucible and its contents are then dried and finally ignited to redness.

ANALYSES BASED ON MEASUREMENT OF GAS VOLUMES

Certain compounds may be estimated by measurement of the volume of gas evolved from a reaction which is known to proceed in accordance with a definite chemical equation. A simple method of collecting the gas is to connect a Hempel gas burette with the reaction vessel as shown in Fig. 15. Alternatively a simple "volumenometer" of the form shown in Fig. 16 may be used. This latter instrument is not well designed to hold mercury, however, and is best kept for the collection of gases which are practically insoluble in ordinary tap water, e.g. nitrogen, hydrogen.

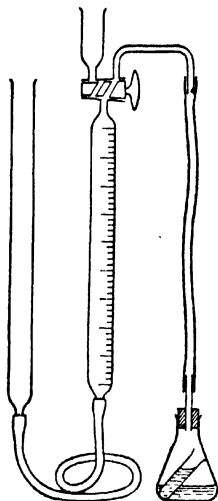


FIG. 15.

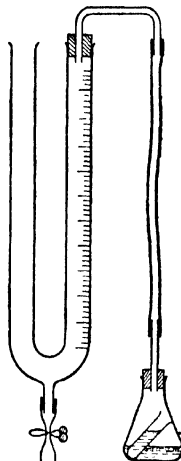
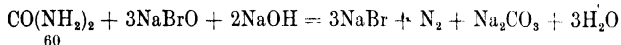


FIG. 16.

It is essential to measure the volume of gas evolved at a known temperature and pressure. The gas is assumed to be at room temperature only if its volume does not change on standing for some time at atmospheric pressure. As the gas collects it is undesirable that a pressure should be developed inside the apparatus; this is avoided by lowering the level of liquid in the second limb.

Estimation of Urea in a Specimen

Urea reacts with a solution of sodium hypobromite in the cold:



From the equation it will be seen that 60 gm. of urea should produce

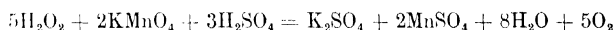
22.4 litres of nitrogen at N.T.P. Urea is, however, partly converted into ammonium cyanate in solution, and the full amount of nitrogen required by the equation is not obtained. Using pure urea it is found that 1 gm., instead of giving $\frac{22,400}{60} = 373$ ml., gives only 357 ml. at N.T.P. The latter figure must therefore be employed.

The sodium hypobromite solution required for the reaction is made by adding 5 ml. of bromide to 100 ml. of 20 per cent. caustic soda solution. The alkali must be kept cold and stirred well while the bromine is slowly added. 30 or 40 ml. of the sodium hypobromite are placed in the reaction flask. Only about 0.1 gm. of urea is required. This may be weighed out by an experienced student on a sensitive balance, but it is more convenient to make up 100 ml. of a 2 per cent. solution by accurately weighing out about 2 gm. of urea and making up a solution in a graduated flask. 5 ml. of the solution may then be taken in a pipette and transferred to the small test tube. This is then placed inside the reaction vessel.

After assembling the apparatus with good rubber connections, the reaction vessel is half immersed in cold water at room temperature for five or ten minutes. After this period the water levels in the gas burette or volumenometer are adjusted to be equal, and the level in the graduated limb is noted. As soon as the reaction is started by tilting the flask the water level in the second limb should be lowered so as to keep the pressure inside the apparatus very nearly atmospheric. The volume of nitrogen collected is read at atmospheric pressure only after the gas has been allowed to cool to room temperature, and no further contraction is observed. The pressure of the nitrogen is obtained by subtracting the saturated vapour pressure of water from the atmospheric pressure. A table of aqueous vapour pressures is given in the appendix.

Estimation of Hydrogen Peroxide

In the presence of dilute sulphuric acid, hydrogen peroxide reacts with potassium permanganate as follows:



Thus, 34 gm. of hydrogen peroxide yield 22.4 litres of oxygen at N.T.P., of which half, in fact, comes from the permanganate. Measurement of the volume of oxygen evolved from a suitable quantity of hydrogen peroxide solution accordingly provides a method of determining the strength of the solution. A Hempel gas burette containing mercury is best for the experiment, but a volumenometer containing dilute sulphuric acid may be used. In either case the oxygen collected is moist.

5 ml. of "20 volume" or 10 ml. of "10 volume" hydrogen peroxide solution are diluted to make 200 ml. of solution. This is then approximately decinormal. 10 ml. of this are placed in a small test tube, which is inserted in the reaction vessel. The vessel itself contains 20 ml. of

decinormal permanganate (the exact strength need not be known), and an equal volume of bench sulphuric acid.

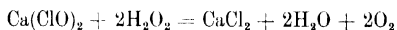
After assembling the apparatus with rubber stoppers the flask is placed up to the neck in a beaker of water at room temperature. After five or ten minutes the mercury levels are adjusted to be equal, and the level in the graduated limb is noted. On tilting the flask so that the reaction begins, oxygen is rapidly evolved and the levelling tube is lowered so that the pressure inside the apparatus remains near atmospheric pressure. The flask must be thoroughly shaken and again cooled to room temperature before the final reading of the gas volume is taken.

The calculation of the weight of hydrogen peroxide in one litre of the original commercial solution, or its "volume strength" (p. 73) should not present any difficulty after the volume of oxygen has been reduced to N.T.P. The mean of two experimental results should be found.

Additional Determinations which may be made with the use of this apparatus are :

1. Estimation of Zinc Dust in a Specimen. Ordinary zinc dust, as used for reduction of ferric salts, contains zinc oxide and a little cadmium, among other impurities. For practical purposes its value can be calculated from the volume of hydrogen evolved when a weighed sample (0.1 gm.) is treated with dilute sulphuric acid (5 ml. of concentrated acid in 25 ml. water). The percentage of zinc present can be calculated, but it should be remembered that any cadmium present will also generate hydrogen. The disadvantage of the method lies in the necessity of weighing only 0.1 gm. accurately.

2. Estimation of Available Chlorine in Bleaching Powder. The nature of bleaching powder has been discussed on p. 82. The hypochlorite present in the substance reacts with hydrogen peroxide in the cold :



half of the oxygen evolved coming from the peroxide. From the relation



it follows that 11.2 litres of oxygen at N.T.P. are equivalent to 71 gm. of chlorine. Allowing for the fact that only half the oxygen evolved comes from the bleaching powder we have 11.2 litres of oxygen at N.T.P. for every 35.5 gm. of available chlorine, or 1 ml. of oxygen at N.T.P. for every 0.00317 gm. of available chlorine.

25 ml. of a suspension of bleaching powder, made as described on p. 82, are placed in the reaction flask. In the test tube are 5 ml. of 10 volume hydrogen peroxide solution. The oxygen should be collected over mercury in a gas burette or over dilute sulphuric acid in a volumeter. The mean of two experimental results should be found.

GENERAL AND PHYSICAL CHEMISTRY.

Determination of the Molecular Weight of a Volatile Liquid from its Vapour Density. Method of Dumas.

In Dumas's method the weight of a given volume of vapour is found by direct weighing. A Dumas bulb of about 100 c.c. capacity is used; this may be of either the older form shown in Fig. 17 (I) or the type shown in (II). The latter is to be preferred for ease of manipulation, and also because an inflammable liquid may be employed as suggested below.

The clean dry Dumas bulb is first weighed full of air. A little of the liquid form of the substance is then introduced by warming and cooling. Not more than 5 c.c. is needed. The liquid is then vaporised when the bulb is heated to a constant temperature, $t^{\circ}\text{C.}$, at least 30° above the

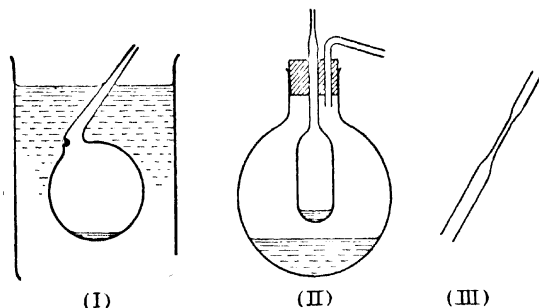


FIG. 17.

boiling point of the liquid. For volatile liquids like chloroform, acetone ether and ethyl bromide, which have boiling points below 70°C. , the liquid used in the outer vessel is water. For higher temperatures a liquid such as toluene (b.p. 110°), commercial xylene (b.p. about 138°) or nitrobenzene (b.p. 210°) may be used in the second type of apparatus fitted with a condenser to regain the solvent.

When the apparatus (I) is used it is essential to depress the Dumas bulb with a stout metal ring held in a clamp or with a special holder, as otherwise the manipulation at 100° becomes awkward. It will be obvious that since the bulb is to be sealed when full of vapour at $t^{\circ}\text{C.}$, the length of projecting stem should be extremely small. It is easier to seal the bulb if a small constriction (Fig. 17 (III)) is made after introducing the liquid.

After the bulb has been heated for about five or ten minutes at the temperature of the boiling liquid in the heating bath, and before sealing off, the presence of vapour issuing from the bulb can be tested for with

a lighted splint. Even with chloroform vapour, which is not inflammable, the behaviour of the flame is a sensitive test. The bulb is sealed when no more vapour is seen to issue from the projecting tube. It is then withdrawn from the heating bath and weighed when cool and dry. If a small piece of tube was detached when sealing this must be weighed with the bulb. A sharp triangular file is then used to make a small scratch on the stem near the tip, and the bulb is held under cold water and opened at this point. The bulb should fill with water and can then be weighed on a rough balance.

Theory.

Let the weight of the bulb full of air at atmospheric temperature and pressure (P cm. mercury) be M_1 gm.

Weight of bulb full of vapour at t° C. and atmospheric pressure (P cm. mercury): M_2 gm.

Weight of bulb full of water: M_3 gm.

The weight of water contained by the bulb is given by $(M_3 - M_1)$, and this is the number of c.c. of air present in the bulb when it was first weighed. Since 1 litre of dry air at N.T.P. weighs 1.2928 gm., the weight (m gm.) of contained air can be calculated. The weight of $(M_3 - M_1)$ c.c. of vapour at t° C. and P cm. pressure is then:

$$M_2 - (M_1 - m) \text{ gm.}$$

and the density of the vapour in gm. per c.c. is then:

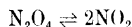
$$\frac{M_2 - (M_1 - m)}{(M_3 - M_1)} \text{ at } t^\circ \text{ C. and P cm. pressure.}$$

$$\text{At N.T.P.: } \frac{M_2 - (M_1 - m)}{(M_3 - M_1)} \cdot \frac{(t + 273) \cdot 76}{273 \cdot P} \text{ gm. per c.c.}$$

This value, divided by 0.00009 (the density in gm. per c.c. of hydrogen at N.T.P.), gives the vapour density.

Notes. 1. It is obviously objectionable to apply the gas laws to vapours in calculating their volumes at N.T.P. For ordinary purposes the error thus introduced is not of practical importance. It must be remembered that molecular weights are usually required to an accuracy of only 5 per cent. or 10 per cent. The method of "limiting densities" obviates this error.

2. When it is desired to find the vapour density of a substance which dissociates on heating, e.g. N_2O_4 , Dumas's method is in general the best. It is, in fact, the only method to use when dissociation produces a change in the number of molecules:



If α is the degree of dissociation, the equilibrium constant K is given by

$$\frac{\alpha^2}{V(1 - \alpha)} = K$$

As will be seen, in Victor Meyer's method (below) there is some dilution of the vapour with air which is an indifferent gas so far as this change is concerned. This means, in effect, an increase in V and consequently there is an increase in the dissociation.

Determination of the Molecular Weight of a Volatile Liquid from its Vapour Density. Method of Victor Meyer.

In this method the volume of vapour provided by evaporation of a known weight of liquid is measured indirectly. A simple form of the apparatus is shown in Fig. 18. Instead of the graduated tube a Hempel gas burette may be used.

The principle of the experiment is quite simple. The central bulb B and the stem of the apparatus are heated by the vapour of the liquid boiled in A. The liquid in the heating bath must have a boiling point which is about 30° higher than the compound to be vaporised. A small quantity of the latter is weighed in a very small bottle, fitted with a ground glass stopper. This is dropped down the apparatus into the bulb B when the conditions inside the apparatus are seen to be steady, i.e. when the *whole of the stem* is heated by the vapour from A to a constant temperature. If a liquid other than water is used a condenser should be attached to the apparatus at the point marked F. It may be necessary to "lag" the apparatus to prevent the vapour from condensing and so not heating the top part of the tube B.

To avoid bumping, a few pieces of porous earthenware should be introduced into A. A little dry sand should be placed in B to break the fall of the bottle. In more expensive forms of apparatus there is some device to avoid opening the apparatus to introduce the bottle. One of these, requiring a ground glass joint, is shown inset.

The measurements required for the determination of the vapour density are the weight of the volatile liquid, the volume of vapour to which this gives rise, and the temperature and pressure of the vapour. The particular point of interest in the method is that the vapour produced when the liquid is placed in the bulb B displaces air equal to its own

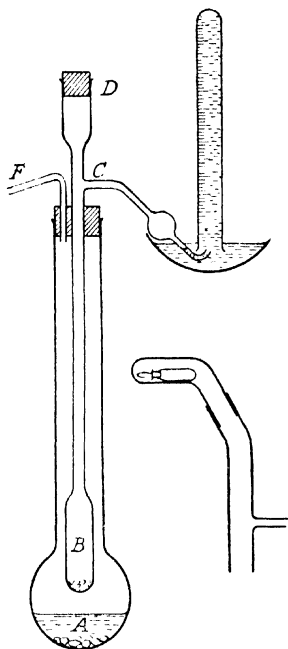


FIG. 18.

volume. This air is driven over into the graduated tube and is collected at the temperature of the cold water in the basin and at atmospheric pressure. To read the volume at atmospheric pressure the tube of air must be transferred to a deep gas jar and then the levels can be suitably adjusted (Fig. 19). If a Hempel burette is used the levelling can be done more conveniently.

a The experimental procedure may now be summarised as follows:

(a) The empty stoppered bottle is weighed.

(b) The bottle is weighed full of the liquid. Difference in weight: m gm.

(c) The heating bath is meanwhile heated to boiling point, the top of the apparatus marked D being left open. After the liquid has been boiling steadily for some minutes and vapour issues from F, the stopper may be inserted. If no bubbles of expanded air are produced the conditions inside the apparatus may be judged to be steady.

(d) The weighed bottle, with its ground glass stopper not too tightly inserted, is dropped from D and the stopper is immediately replaced. After a few seconds bubbles of air will be seen to collect in the graduated

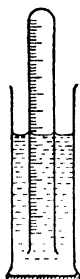


FIG. 19.

tube which must be in position.

(e) When no more air bubbles are produced the volume of the air collected and its temperature ($t^{\circ}\text{C.}$) and pressure must be recorded. As mentioned above, the air should be measured at atmospheric pressure. Alternatively the height of the water (in cm.) in the graduated tube may be recorded. If this height is h cm. the air is measured at $\left(P - \frac{h}{13.6}\right)$ cm.

of mercury. This, however, is not the partial pressure of the air since water vapour is present. The saturated vapour pressure (p cm.) of water at the temperature of the air can be found from the table in the appendix (it is there given in mm.).

Let the volume of air collected be V c.c. and the atmospheric pressure be P cm. mercury. Assuming that no correction for difference in water level is needed and that the volume is read with the levels equal, the pressure of air is given $(P - p)$. The volume at N.T.P. is then

$$\frac{273}{(273 + t)} \cdot \frac{(P - p)}{76} \cdot V \text{ c.c.}$$

The density in gm. per c.c. is then given by

$$\frac{m \cdot (273 + t) 76}{V(P - p) 273} \text{ gm. per c.c. at N.T.P.}$$

The vapour density is then:

$$\frac{m \cdot (273 + t) 76}{V(P - p) 273 \cdot 0.00009}$$

Notes. 1. It may be questioned why the volume of vapour is considered to be the same as the volume of air at t° and not at the temperature of the heating bath. While it is true that the air displaced is at the higher temperature, this air is cooled on passing into the graduated tube and undergoes a contraction. Inefficient heating of the stem of the apparatus is the commonest cause of poor results.

2. The method is not used for finding the vapour density of substances which dissociate with a change in the number of molecules. The reason for preferring Dumas's method has been explained on p. 108.

Determination of the Molecular Weight of a Substance in Solution from the Depression of Freezing Point. Beckmann's Apparatus.

Raoult's Law for the effect of a dissolved substance in lowering the vapour pressure of a solvent may be expressed in the form :

$$\frac{p_0 - p_s}{p_0} = \frac{n}{N + n}$$

where p_0 is the saturated vapour pressure of the solvent and p_s that of a dilute solution at the same temperature, N is the number of molecules

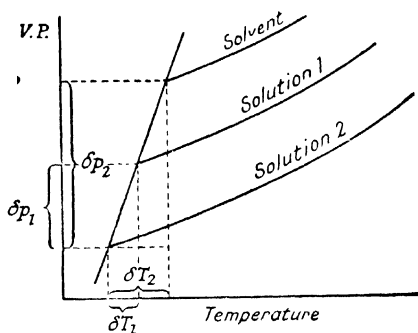


FIG. 20.

of solvent per unit volume, n that of solute per unit volume. This means that equimolar solutions of different substances in the same solvent will have the same effect in lowering the vapour pressure. This, of course, applies to non-electrolytes only. Experiment shows that for weak solutions the lowering of freezing point of a solvent is directly proportional to the lowering of vapour pressure. This will be clear from Fig. 20, which shows that, since the V.P./Temp. curves are parallel,

$$\frac{\delta p_1}{\delta p_2} = \frac{\delta T_1}{\delta T_2}$$

The curves are shown intersecting the V.P./Temp. curve for the solid solvent. The points of intersection are of course the f. pts. It follows

that, in the case of non-electrolytes, if there are w gm. of solute in 1000 gm. of solvent and M is the molecular weight of the solute,

$$\delta T = K \frac{w}{M}$$

where K is the "molecular lowering," i.e. the lowering produced (theoretically) by one gram-molecule of any substance in 1000 gm. of solvent.

Setting aside the "anomalous" results produced by electrolytes it is necessary to point out that Raoult's law applies only to ideal solutions, that is, to those in which no compound formation between solute and solvent takes place. Even where this would appear to be absent certain anomalous cases are known. The better known examples are carboxylic acids in non-hydroxylic solvents, certain phenols in benzene and nitrobenzene in benzene. If these are avoided the method gives excellent values for the molecular weights of substances in solution, provided no association or dissociation occurs. The molecular depressions of some solvents are given in the table.

<i>Solvent.</i>	<i>F. pt.</i>	<i>K for 1000 gm.</i>	<i>Density (gm./c.c.)</i>
Water	0° C.	1.85 ²	1.0
Benzene	5.5	5.12	0.88
Glacial acetic acid	17.0	3.90	1.08
Ethylene dibromide	9.0	11.80	2.2
Nitrobenzene	5.72	7.0	1.2
Camphor *	175	40.0	"

* See Rast's method below.

Experimental Method. The apparatus is shown in Fig. 21. Except in the case of Rast's method the depressions to be measured are only a fraction of a degree, and for this reason a special thermometer capable of showing a temperature difference of $\frac{1}{100}$ th of a degree was invented by Beckmann. This thermometer has a range of only six degrees, and is set for a particular range of temperature beforehand. This is described below.

A known weight of solvent is placed in the middle tube C in the figure, and this is insulated by an air space from the cooling bath A. Without this air space the rate of cooling would be too rapid and not sufficiently uniform. The freezing point of the solvent on the Beckmann thermometer is first determined; then a weighed quantity of solute is introduced through the side tube D, a clear solution is obtained, and the freezing point is again found. The most important point of technique in the use of the apparatus is that the freezing point is always approached from *below* after a small degree of supercooling has been produced. Solidification is then induced and the highest temperature then reached is taken to be the freezing point. If the freezing point is approached from above small fluctuations of temperature take place even while the solvent is solidifying.

Setting a Beckmann thermometer. If the solvent used is, for example, benzene (f.p. 5.5° C.) the Beckmann thermometer will be suitably adjusted if the mercury ends somewhere about the middle of the scale when the

temperature is actually 5.5°C . To adjust the thermometer a large beaker of water at about 8° or 9° is required. The next step is to get the mercury thread of the thermometer to extend from the bulb to the reservoir at the top. (See that the Beckmann thermometer is made for low temperatures: a Beckmann thermometer for boiling points contains less mercury. The instrument will have this marked on its back.) It may be necessary to place the bulb of the thermometer in hot water. By inverting the thermometer smartly the thread must be made to join up with the mercury in the reservoir.

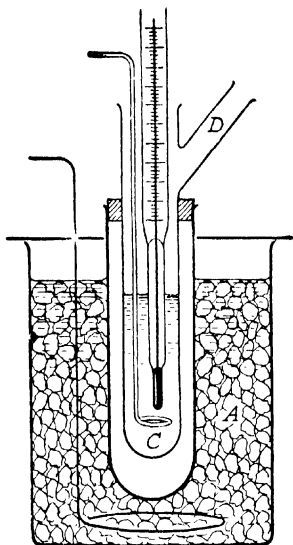


FIG. 21.



FIG. 22.—Reservoir of Beckmann thermometer.

With the thermometer in the upright position and a continuous thread from top to bottom, the bulb is then lowered into the water at 8° or 9° . This causes mercury to be drawn down into the bulb. After a minute or two the upper end is given a smart tap with the tips of the fingers, and this will jerk the reserve mercury off the mercury at the end of the capillary. When the bulb is wiped on filter paper and lowered into benzene at about 6° the mercury will end on the upper half of the scale.

Finding the freezing point. The cooling bath should contain a mixture of water and ice. This is occasionally stirred. 50 c.c. of pure benzene are transferred to the tube C, using a pipette. The weight of benzene is then calculated (densities given on p. 112). The Beckmann thermometer is lowered into the benzene and the reading of the thermometer is observed.

It is important to know approximately where the mercury will stand when the temperature is 5.5°C . The benzene is not stirred while the temperature is falling, until it is clear that the temperature is lower than the freezing point by about 0.5° . At this point the benzene is stirred steadily until crystallisation begins to take place. The temperature shown on the Beckmann thermometer will then begin to rise. The highest temperature recorded is noted as the freezing point. A redetermination of the temperature can be carried out quite quickly if the inner tube is lifted and the benzene is warmed by the hand until it is again liquefied. The mean of three determinations should be found.

0.5 to 1.0 gm. of the solid solute is then weighed out into a clean dry weighing bottle or specimen tube. The inner tube, C, is again lifted out and the solute is dropped into the benzene through the side tube. The mixture is warmed by the hand until a clear solution is obtained. The determination of the freezing point is then carried out in the same way as before. Once again the mean of three determinations should be found. The separate readings should not differ from the mean by more than 0.01° . Using a hand lens greater accuracy in reading the thermometer can be attained.

The molecular weight is obtained by substitution in the formula. In the case of benzene the molecular weight is given by

$$M = \frac{5.12w}{T}$$

where w is the weight in grams of solute in 1000 gm. of benzene.

Rast's Method. It will be observed that camphor has an exceptionally high molecular lowering (p. 112). It is possible, therefore, to determine freezing point depressions produced by substances which are soluble in camphor with an ordinary thermometer graduated in $\frac{1}{2}$ ths of a degree. In this case it is the melting point and not the freezing point which is observed, the usual method for finding melting points being used.

About 5 gm. of camphor are weighed in a weighed test tube. A few crystals of the solute are then added, and the weight is accurately redetermined. The mixture is then heated carefully in the Bunsen flame until a clear solution has been obtained. The solution is then allowed to solidify, and is then scraped out on to a piece of clean paper. Two melting point tubes (p. 158) are then filled (*a*) with pure camphor, and (*b*) with the solidified solution. These are placed side by side on the thermometer in the melting point bath. The two melting points are then carefully determined. The molecular weight is calculated in the same way as for the Beckmann method.

Determination of the Molecular Weight of a Substance in Solution from the Elevation of Boiling Point. A modified form of Landsberger's Apparatus.

It is of importance that the elevation of boiling point of a solvent by the presence of a dissolved (solid) solute is directly proportional to the

lowering of vapour pressure. For dilute solutions the curves showing the change of vapour pressure with temperature are of the form shown in Fig. 23. Since these are parallel

$$\frac{\delta p_1}{\delta p_2} = \frac{\delta T_1}{\delta T_2}$$

This means that the effect is proportional to the molecular concentration, i.e. equimolar solutions will have the same effect in raising the boiling

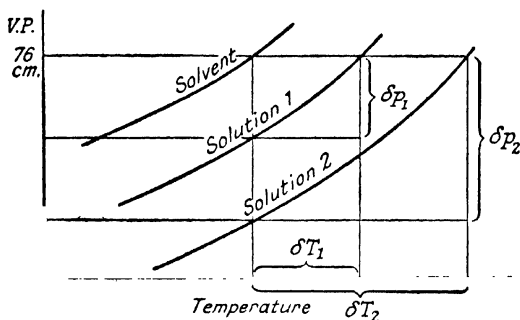


FIG. 23.

point. The equation relating the elevation of boiling point with the molecular weight is therefore of the same form as that for the depression of freezing point (p. 112), i.e.

$$\delta T = K \frac{w}{M}$$

where K is the molecular elevation produced by one gram-molecule of solute dissolved in 1000 gm. of solvent. The values for the solvents given in the table will be seen to be somewhat smaller than the molecular lowerings given on p. 112. A Beckmann thermometer, made for boiling point determinations, is accordingly used.

Solvent.	B. pt.	K for 1000 gm.	K' for 1000 c.c. at the B. pt.
Water	100° C.	0.52°	0.54°
Chloroform	61.2	3.88	2.77
Acetone	65.2	1.72	2.22
Benzene	80.2	2.57	3.15
Ethyl alcohol	78.5	1.15	1.56

In the modified form of Landsberger's apparatus shown in Fig. 24, solvent is placed in the boiler A and in the graduated tube B. Vapour from A bubbles through the liquid in B and brings it to the boiling point. A condenser may be attached at C when liquids other than water are used. The boiling point, as shown on the scale of the Beckmann ther-

meter, is read and then a weighed quantity of the solid solute is added to the solvent in B and the boiling point is redetermined. It should be clear that since the solution has a lower vapour pressure than the solvent at the temperature of the vapour from the boiler, vapour will condense in B and give up latent heat until the temperature is raised to the boiling point of the solution.

With this type of apparatus the boiling point of the solution and its volume must be found simultaneously since the solution is being progressively diluted. In order to read the volume it is in practice necessary to

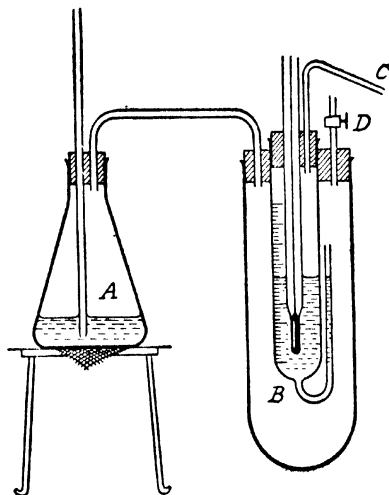


FIG. 24.

open the tap D momentarily, so that a level meniscus can be observed. Several readings can be made of both volume and boiling point in the course of about quarter of an hour.

The procedure is therefore as follows :

(a) The Beckmann thermometer is adjusted so that the mercury thread will end on the lower half of the scale. For this purpose a beaker of liquid at a temperature some 3° or 4° above the required temperature is needed. The details have been described on p. 112.

(b) The boiling point of the pure solvent is found on the Beckmann thermometer. C

(c) A known weight (about 0.5 to 1.0 gm.) of solute is added to the solvent in B and the new boiling point is determined. The volume is found simultaneously.

Conductivity of Electrolytes.

The measurement of electrical conductivity of a solution offers perhaps the most direct approach to the study of electrovalent compounds. Although the oppositely charged ions are strongly attracted to one another there is no real "bond"; the passage of a direct current brings about a separation. The relation between the direct current (I) and the applied potential difference (V) is, in general, of the form shown in Fig. 25. The size of the "decomposition voltage," represented by V_0 , depends on the nature of electrolyte and the electrodes. Polarisation effects must be minimised in measurements of conductivity. For this reason (i) platinum surfaces coated with platinum black are commonly used, and (ii) a high frequency alternating current is used. Any polarisation due to deposition at the electrodes and changes in concentration is thus almost completely avoided.

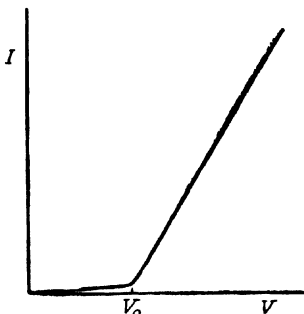


FIG. 25.

The specific conductivity (k) of a solution is the reciprocal of the specific resistance (σ). A conductivity cell of a more or less standard

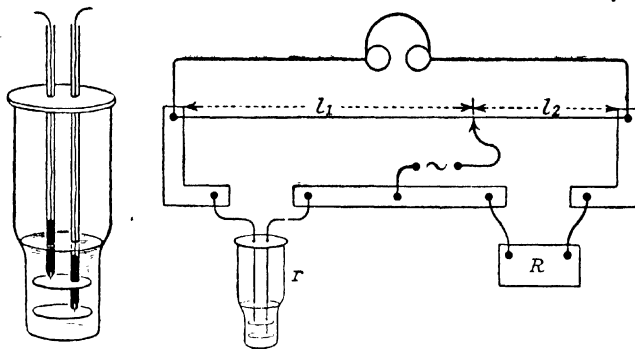


FIG. 26.

pattern is employed. Fig. 26 shows one common type of cell and the modified Wheatstone Bridge circuit used. As a source of alternating current one may use either

- (a) a valve oscillator (with usually a stage of amplification), or
 (b) a small induction coil. This does not give true A.C., but disconnecting the condenser produces an improvement.

The theory of the circuit is the same as that for the ordinary Wheatstone Bridge. When the point of balance is found, so that the note heard in the headphones practically disappears, we have :

$$\frac{l_1}{l_2} = \frac{r}{R}$$

where r is the resistance of the solution in the cell, and R is a suitable standard resistance (found by removing plugs from the resistance box). Fuller details of the bridge are given in textbooks of electricity.

The Cell Constant. All measurements of the resistance of solutions must be carried out with the cell in a thermostat since there is, in general, a change of about 2 per cent. in the resistance for 1° C. change in temperature. A temperature of 18° is very convenient (cf. table of ionic mobilities for this temperature below).

The specific resistance is defined as the resistance between the opposite faces of a unit cube of a substance. Since it is impracticable to make electrodes exactly one square centimetre in area and exactly 1 cm. apart the *cell constant* must be found, i.e. the constant by which the resistance must be multiplied to obtain the specific resistance. For this purpose $\frac{N}{50}$ KCl made up in conductivity water * may be used. The specific conductivity of this solution has been accurately found for a range of temperature. If the resistance of $\frac{N}{50}$ KCl in the cell is r ohms at a given temperature, the conductivity is $1/r = c$ (in reciprocal ohms or mhos).

Temperature. °C.	Sp. conductivity (k) of $\frac{N}{50}$ KCl.
10	0.001996
15	0.002143
18	0.002395
20	0.002501
25	0.002768

The cell constant (K) is then found from the relation

$$K = \frac{k}{c} = kr$$

Once the cell constant K has been determined great care must be taken not to deform the electrodes or alter the distance between them. When not in use the cell should be kept full of conductivity water.

* Distilled water, made alkaline with caustic soda and redistilled with a little potassium permanganate, using a copper tube condenser, is suitable. Only the middle fraction is retained. A hard glass condenser tube can be used instead.

The Equivalent Conductivity and Degree of Dissociation of a weak Electrolyte ($\ln \frac{N}{10}$ solution).

The equivalent conductivity, Λ_V , of a solution containing one gram-equivalent of solute in V litres is given by

$$\Lambda_V = 1000 kV \text{ (reciprocal ohms)}$$

This quantity shows an increase with V in all cases and for strong electrolytes, when V is greater than 1000, the equivalent conductivity reaches a maximum and constant value so that further dilution has no (appreciable) effect. This conductivity at "infinite dilution" corresponds on the original Arrhenius theory to complete ionic dissociation. At any ordinary dilution, then, the "conductance ratio," Λ_V/Λ_∞ , is a direct measure of the "degree of dissociation" (α)—according to the original Arrhenius theory. According to modern ideas the variation of α with

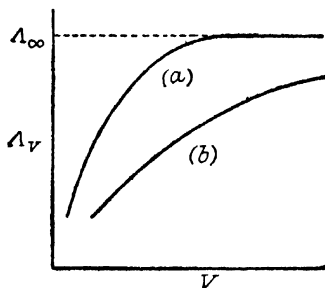


FIG. 27.

(a) Strong electrolyte. (b) Weak electrolyte.

Λ_V is due more to change in ionic speeds than to a change in the number of ions carrying the current. We obtain the degree of dissociation from the conductance ratio, therefore, only in the case of weak electrolytes for which the equilibrium between ions and an undissociated molecule does seem to exist. It will be seen, however, from Fig. 27 that, although the equivalent conductivity does increase with dilution, the value at infinite dilution cannot be found by direct measurement. At great dilutions the conductivity of such solutions is extremely low and a constant result cannot be found.

Only one measurement (that of Λ_V) is therefore made in obtaining the degree of dissociation. The apparatus required in the previous section is assembled. Some decinormal electrolyte is placed in the conductivity cell. Acetic acid, oxalic acid, succinic acid or ammonium hydroxide are suitable electrolytes. Conductivity water is used in making up the solution. (The solution is kept at 18°.)

To find the conductivity at infinite dilution we must apply Kohlrausch's law of independent mobility of ions. For acetic acid, for example, we have

$$\Lambda_{\text{HAc}} = \Lambda_{\text{H}^+} + \Lambda_{\text{Ac}^-}$$

these being the conductances at infinite dilution. The conductances (or mobilities) are as follows, for the electrolytes mentioned above :

<i>Ion.</i>	<i>Mobility (18° C.).</i>
H ⁺	313.9
NH ₄ ⁺	64.7
OH ⁻	174.0
Ac ⁻	35.0
$\frac{1}{2}\text{Ox}^-$	63.0

Having found the value of Λ_v the value of Λ_∞ is found, as shown above.

The Change of Equivalent Conductivity with Dilution for a strong Electrolyte.

According to the theory of strong electrolytes due to Debye and Huckel, the complete dissociation of a strong electrolyte is to some extent masked by attractions between oppositely charged ions. This leads to the practical immobilisation of a certain proportion of ions at any instant. The mobility of the ions, in carrying an electric current, is therefore reduced by a kind of electric viscosity. On dilution, the ions being further apart, this effect is reduced and the equivalent conductivity increases.

For an electrolyte of the form B'A⁻ the equation due to Debye and Huckel requires that the equivalent conductivity shall change with dilution according to an equation of the form

$$1 - \frac{\Lambda_v}{\Lambda_\infty} = K\sqrt{C}$$

and Onsager's equation for uni-univalent electrolytes also requires that Λ_v/Λ_∞ shall vary with the square root of the concentration. This relation may be tested over the range from 0.1 N to 0.01 N, using a strong electrolyte such as potassium chloride. The apparatus is as described previously. The conductivity cell must, of course, be kept at a constant temperature in a thermostat, and every care must be taken to ensure accuracy in the measurements. A valve oscillator is very desirable.

Starting with 50 c.c. of 0.1 N potassium chloride in the cell, 10 c.c. are withdrawn after doing the first measurement and replaced with 10 c.c. of conductivity water. Next, 25 c.c. are withdrawn and replaced with water, and this is repeated so that the following concentrations are obtained :

0.1 N	replace 10 c.c.
0.08	replace 25 c.c.
0.04	replace 25 c.c.
0.02	replace 25 c.c.
0.01	

A methodical way of entering up results should then be followed. The following is suggested :

Concentration (C)	Bridge reading (<i>l</i>)	Resistance (<i>r</i>)	Sp. conductivity $k = K/r$

from which is obtained :

Concentration (C)	Vol. in litres of 1 gm. equiv. (V)	Equiv. Conductivity $\chi_v = 1000 kV$	\sqrt{C}

As an alternative to plotting χ_v against \sqrt{C} , χ_v may be plotted against V when a graph of the form shown on p. 119 is obtained. The results obtained must be regarded as a good test of the accuracy and care with which the experiment has been done. There should be a steady increase in the values tabulated under χ_v . Erratic results are a sure indication of poor experimental conditions. The resistance of the cell, when containing nothing but conductivity water, should be found as a check on the purity of the water. A resistance of 10,000 ohms should then be needed in the circuit. When using the potassium chloride solutions, 100 ohms will be sufficient to obtain balance points on the middle part of the bridge wire.

The graph of χ_v against \sqrt{C} is approximately linear over the range suggested. Extrapolation will give the value of the equivalent conductivity at infinite dilution ($\sqrt{C} = 0$).

Transport Numbers

The fact that equal amounts of + and - charge are given up in unit time at the electrodes during electrolysis does not mean that in general the cation and anion move with equal speeds. This point is explained in textbooks of Physical Chemistry. If the electrodes are not themselves sources of new ions during electrolysis, there will in any case be a lowering of the concentration of the solute around the electrodes; it is the

* The cell constant (K) is found as described on p. 118.

difference in the losses at the two electrodes which is explained by the difference in speed. It may be shown quite simply that:

$$\frac{\text{decrease in conc. of solute at anode}}{\text{decrease in conc. of solute at cathode}} = \frac{\text{speed of cation}}{\text{speed of anion}}$$

Writing these decreases of concentration δC_1 and δC_2 , if a fraction n of the total current passing is carried by the anion and $1 - n$ is carried by the cation, we have

$$\frac{\delta C_1}{\delta C_2} = \frac{v}{u} = \frac{1 - n}{n}$$

where v and u are the speeds of the cation and anion respectively. The

actual values of v and u depend on the potential gradient employed, and we therefore determine n and $1 - n$ from the observed changes in concentration. These are the "transport numbers" of the anion and cation respectively. Their significance is that we can divide the equivalent conductivity of a salt at infinite dilution in the proportion of the two transport numbers:

$$nA_\infty \text{ and } (1 - n)A_\infty$$

which are, of course, the ionic mobilities (Kohlrausch). From the mobilities the absolute velocities can be found.

There are various forms of transport apparatus, all of which are designed to restrict the change of concentration to the electrode compartments. It is a fundamental assumption that no change of concentration takes place between the electrodes.

To determine the transport number

for the silver ion in a solution of silver nitrate the simple apparatus shown in Fig. 28 is adequate. It is filled with a solution of about $\frac{N}{10}$ or $\frac{N}{20}$ strength and connected in series with a rheostat, copper voltameter (not shown in figure) and a milliammeter. A direct current supply of about 50 volts is required to set up a current of about 10 milliamps. The magnitude of the current depends on the dimensions of the electrodes, etc. This current must be maintained steady for about 1 or 2 hours, and the total time is recorded. From the change in weight of the cathode of the voltameter the total charge passed during the experiment may be determined.

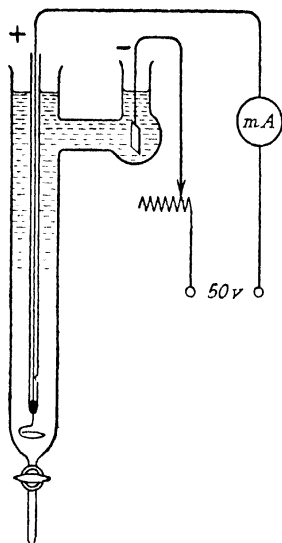


FIG. 28.

To find the change in concentration around the anode about as much solution as would fill the anode limb is run out immediately the current is switched off. It is run into a weighed flask and the amount determined by weighing. The silver nitrate present is then found by a careful titration with standard ammonium thiocyanate (Volhard's method). A titration of a known *weight* of the original silver nitrate solution must also be done during the experiment.

The calculation of the transport number may be explained as follows: From the titrations calculate the number of gram-equivalents of silver ion which are associated with a given weight of water in the two cases (the weight of water in the anode compartment);

i.e. before electrolysis W gm. of water associated with x gm.-equivs. of silver;

after electrolysis W gm. of water associated with y gm.-equivs. of silver.

Increase in amount of silver present: $y - x$ gm.-equivs.

Let total weight of copper deposited be m gm.-equivs.

i.e. m gm.-equivs. of silver have been deposited.

The increase in the anode compartment is, of course, not as great as m since silver ions have been leaving the anode compartment. The difference between m (which would have been the increase if there had been no transport by silver ions) and the increase observed represents the amount which has left the compartment.

$$\therefore \frac{m - (y - x)}{m} = \text{fraction of current carried by Ag}^+ \text{ ion.}$$

This is the required transport number. The transport number for the nitrate ion is then found since the sum of the two numbers is 1. The concentration of the solution should be recorded.

The equivalent conductivity at infinite dilution (Λ_∞) for silver nitrate is 116.1. From this the mobilities of the two ions can be found since

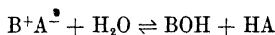
$$u_c = (n - 1)\Lambda_\infty \quad \text{and} \quad v_a = n\Lambda_\infty$$

The accepted values are: $\text{Ag}^+ \quad u_c = 54.02$
 $\text{NO}_3^- \quad v_a = 61.78$

It is interesting to compare these with the mobility of the hydrogen ion (347.2), and hydroxyl ion (174). The reason for the high mobility of the hydrogen ion has been discussed by Speakman (*Valency*, p. 35).

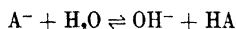
Degree of Hydrolysis. Strengths of Acids and Bases

As mentioned on p. 15, hydrolysis is the outcome of the strong dissociation of salts of even weak acids or bases, coupled with the feeble dissociation of the acids and bases themselves. In the reaction represented:



the position of equilibrium depends on the strength of the acid HA or

the base BOH (or both). In the case where the hydroxide BOH is strong base we have:



The hydrolysis constant K_h is given by

$$\frac{[HA][OH^-]}{[A^-]} = K_h,$$

$[H_2O]$ being constant for a dilute solution. If from 1 gm.-equivalent (in V litres) a fraction α gm.-equiv. of the acid HA is formed, we have

$$[HA] = [OH^-] = \frac{\alpha}{V}$$

and

$$[A^-] = \frac{1 - \alpha}{V}$$

Hence

$$K_h = \frac{\alpha^2}{V(1 - \alpha)}$$

and, if α is small,

$$K_h = \frac{\alpha^2}{V}, \text{ i.e. } \alpha \simeq \sqrt{K_h V}$$

Now

$$[H^+][OH^-] = K_w$$

and

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

Dividing:

$$\frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]} = K_h$$

Hence

$$\alpha \simeq \sqrt{\frac{K_w}{K_a} V} \quad (i)$$

This equation shows the relation between the degree of hydrolysis α and the dissociation constant of the weak acid provided α is small. We can find α since

$$[OH^-] = \frac{\alpha}{V}, [H^+] = \frac{K_w}{[OH^-]} = \frac{K_w V}{\alpha}$$

i.e.

$$\alpha = \frac{K_w V}{[H^+]} \quad (ii)$$

It follows from (ii) that if we can find $[H^+]$ for the solution, α can be found. For a N solution $V = 1$. Knowing α the dissociation constant K_a can be found from equation (i). It should be clear that if N solutions of a series of sodium salts are made, the hydrogen ion concentration gives us a rough means of comparing the strengths of the acids.

Determination of pH by means of indicators. A series of approximately N solutions is made up. (The method is not capable of great accuracy.) 250 c.c. of each solution is sufficient and if placed in stoppered bottles, labelled with the name of the solution, these may be kept permanently for this experiment.

To determine the hydrogen ion concentration an indicator or series of indicators is used. A set of standard tubes containing suitable buffer solutions and showing the colour of the indicators over a range of pH values is required. For this the B.D.H. "Capillator" outfit is most convenient since one indicator is used for a wide range of pH values. To carry out a determination with an indicator for which standard tubes are available, it is simply necessary to mix a few drops of the salt solution with a few drops of indicator on a watch glass and then to compare the colour developed with the colours of the standard tubes. Using the "Capillator" a capillary tube full of the salt solution coloured suitably deeply with indicator is all that is needed.

Suitable solutions are:

(a) Comparison of the strengths of some weak acids: sodium acetate, formate, chloracetate, cyanide and phenate.

(b) Comparison of the strengths of weak bases: ammonium chloride and aniline hydrochloride are suitable. For this group of solutions we have in place of equations (i) and (ii) above:

$$\alpha = \frac{K_w V}{[OH^-]} \text{ and } \alpha = \sqrt{\frac{K_w V}{K_b}}$$

Titration of a Weak Acid with a Strong Alkali. The Henderson Equation.

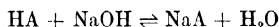
If a weak acid is titrated in dilute solution with a strong alkali it is possible to calculate how the hydrogen ion concentration will change as the alkali is added. It is necessary to assume

(i) that the alkali is completely dissociated, and

(ii) that the dissociation of the acid is repressed by the salt formed according to the usual mass action ideas.

If the alkali is run into the acid we may take the amount of acid present in one litre to be (i) a gm.-mols. initially, and (ii) b gm.-mols. at any subsequent instant.

From the equation



it follows that when $[HA] = b$, $[Na^+] = b$ (i)

and $[HA] + [A^-] = a$ (ii)

We also have, from the electrical neutrality of the solution:

$$[Na^+] + [H^+] = [A^-] + [OH^-] \quad (iii)$$

and, for the dissociation constant of the acid:

$$\frac{[H^+][A^-]}{[HA]} = K \quad (iv)$$

From (iv) and (ii):

$$[H^+] = K \frac{a - [A^-]}{[A^-]}$$

and from (iii) and (i):

$$[H^+] = K \frac{a - b - [H^+] + [OH^-]}{b + [H^+] - [OH^-]}.$$

Since, up to the point of neutrality, $[OH^-]$ is a small quantity, it may be ignored. Whence:

$$[H^+] = K \frac{(a - b) + [H^+]}{b + [H^+]}$$

If, as is here the case, $[H^+]$ is small, the equation may be reduced to

$$[H^+] = K \frac{(a - b)}{b} = K \frac{[\text{acid remaining}]}{[\text{salt formed}]}$$

$$\text{or: } \log [H^+] = \log K + \log \frac{[HA]}{[NaA]}$$

$$\text{or: } pH = \log \frac{[\text{salt}]}{[\text{acid}]} - \log K \text{ (the Henderson equation)}$$

For acetic acid $K = 1.86 \times 10^{-5}$. If, then, 50 ml. of Normal acetic acid are placed in a beaker and Normal caustic soda is run in from a burette, the pH of the solution may be found, after the addition of each 10 ml. of alkali, with the use of the B.D.H. capillator. The result may be compared with the value calculated on the Henderson equation. There is only fair agreement in the example chosen.

It is desirable to have exactly Normal caustic soda for the experiment, so as to simplify the calculation of the concentrations. The first step is then to titrate the alkali against the acid, using phenolphthalein indicator, so as to find its normality. The acid must then be diluted to be exactly Normal (so that it should first be rather stronger). 50 ml. of one solution will now require 50 ml. of the other (decinormal solutions may be preferred).

Starting with a burette full of N caustic soda, the 50 ml. of acetic acid are placed in a beaker. It is then easy to withdraw a capillary tube full of the solution after the addition of each 10 ml. of alkali. The pH of the solution is found with the use of the B.D.H. indicator or any other "universal" indicator giving a range from $pH = 4$ to $pH = 10$ or 11. The results of the experiment are best shown in tabular form:

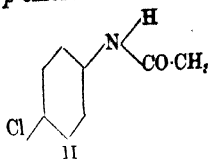
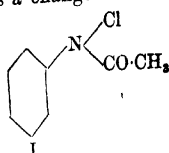
ml. NaOH added.	Total volume.	[salt].	[acid].	pH	Observed pH
0	50				
10	60				
20	70				
30	80				
40	90				
50	100				

* This value can be calculated from the relation $[H^+] = \sqrt{KV}$ (the Ostwald dilution law).

† This value can be calculated from the relation $[H^+] = \sqrt{K_w KV}$ where K_w is the ionic product for water, viz. 10^{-14} (cf. equation (i), p. 124).

The Law of Mass Action. The Rate of Transformation of N-Chloroacetanilide.

N-chloroacetanilide (I) in the presence of acid and in aqueous solution undergoes a change * into the isomeric *p*-chloroacetanilide (II).



According to the Law of Mass Action (p. 6), the rate at which this change proceeds is at any instant proportional to the concentration of I. Since I is progressively changing into II the rate of change falls off. If there were a gm.-mols. per litre of I originally, and after a time t , x gm.-mols. have been transformed, the rate of transformation will be given by

$$\frac{dx}{dt} = k(a - x)$$

or :

$$\frac{dx}{a - x} = k \cdot dt$$

Integrating :

$$-\log_e (a - x) = kt + C$$

Since $x = 0$ when $t = 0$, $-\log_e a = C$

$$\therefore \frac{2.303}{t} \log_{10} \frac{a}{a - x} = k$$

So long as a and $(a - x)$ are measured in units which are proportional to the molecular concentrations the latter need not be found.

In this case the course of the reaction may be followed by withdrawing 5 c.c. portions of the solution and adding excess acidified potassium iodide. The standard thiosulphate needed to titrate the iodine liberated gives a direct measure of the quantity $(a - x)$.

Required :

10 gm. N-chloroacetanilide (preparation on p. 194).

50 c.c. 20 per cent. acetic acid.

50 c.c. N hydrochloric acid.

6 small flasks, each containing 10 c.c. potassium iodide solution.

$\frac{N}{10}$ sodium thiosulphate.

The N-chloroacetanilide is dissolved in the acetic acid and the solution, in a 250 c.c. flask, is placed in a thermostat or a large vessel of water at room temperature. The hydrochloric acid is also placed in a flask and kept at the same temperature. After a period to attain the temperature of the thermostat the hydrochloric acid is poured into the N-chloroacetanilide solution. At this instant a stop-clock is set going.

The first iodine estimation is done immediately after mixing; 5 c.c. of the solution are withdrawn in a pipette and added to 10 c.c. of potas-

* There is no doubt that a reaction with the acid takes place and that the change is really a pseudo-unimolecular one.

sium iodide solution *just previously* acidified with hydrochloric acid. The iodine liberated is then titrated with decinormal sodium thiosulphate solution, using starch solution indicator. The titre is noted. At ten-minute intervals this procedure is repeated, but after half an hour the rate of change is much reduced and it is unnecessary to do more than one more at the end of an hour. We then have:

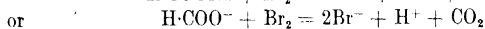
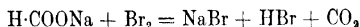
Time in minutes.	Titre of thiosulphate $\frac{N}{10}$
0	n_0
10	n_1
20	n_2
30	n_3
60	n_4

On plotting $\log. \frac{n_0}{n}$ against t the points should fall approximately on a straight line.

Note. The N-chloroacetanilide used in this experiment must have the correct m.p. (91°C.). The yield of the compound after it has been recrystallised (p. 194) is not high, and an experiment requiring much more accessible materials is described below.

Law of Mass Action. Reaction of Bromine with Formic Acid.

Sodium formate and bromine water are the principal chemicals required in this experiment. These substances react in solution in the following way:



Halogen-substituted formic acids are too unstable to be isolated, but are known in the form of esters.

If a large excess of formate ion is present the rate of the reaction at any instant depends on the concentration of bromine remaining,

$$v = k[\text{Br}_2]$$

i.e. the reaction is now a "pseudo-unimolecular" one with respect to bromine. The concentration of bromine at any instant can be determined by withdrawing a small sample in a pipette, liberating iodine from acidified potassium iodide, and titrating with standard thiosulphate. Only very dilute solutions are used.

Required:

Bromine water diluted to ten times its volume (a pipette must *not* be used here).

Sodium formate. 7 gm. per litre.

N sulphuric acid.

Sodium thiosulphate. 2.5 gm. per litre $\left(\text{approximately } \frac{N}{100}\right)$.

6 small flasks containing 10 c.c. potassium iodide $\left(\text{about } \frac{N}{10}\right)$

and a little starch solution.

100 c.c. of the dilute bromine solution are transferred from a measuring cylinder to a small conical flask. This is then stoppered and kept in a large vessel of water at room temperature. 200 c.c. of the formate solution and 100 c.c. of the Normal acid are then mixed in a large conical flask which is also kept at room temperature.

When the bromine solution is poured into the large conical flask a stop clock is set going and 50 c.c. of the mixture is immediately withdrawn, using a pipette. (Provided ordinary care is taken this very dilute solution can be taken in a pipette.) The 50 c.c. portion is quickly transferred to one of the flasks containing potassium iodide and starch. The iodine liberated is then titrated with the $\frac{N}{100}$ thiosulphate. Less than 10 c.c. will be required. The process of estimating bromine is repeated every five minutes for half an hour.

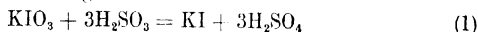
As in the previous example (experiment on N-chloracetanilide) we may write the expression for the unimolecular constant in the form :

$$\frac{2.303}{t} \log_{10} \frac{n_0}{n} = K$$

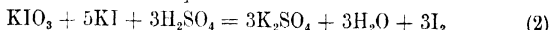
where n_0 is the titre at the beginning of the experiment and n any particular value subsequently. By plotting $\log. \frac{n_0}{n}$ against t (in minutes) a straight line relation should be obtained.

Law of Mass Action. The Reaction between Potassium Iodate and Sulphurous Acid.

Potassium iodate oxidises sulphurous acid to sulphuric acid, the simplest representation being :



This change is catalysed by hydrogen ions and proceeds at a measurable rate in feebly acid solution. As soon as all the sulphite ion has been oxidised, *but not before*, the excess iodate reacts with the iodide present according to the well-known equation :



Since reaction (2) is practically instantaneous the liberation of iodine is the sign that reaction (1) is completed. In the presence of starch solution a dark blue colour suddenly develops. At a given temperature the rate of the first reaction depends on the concentration of the iodate, the sulphurous acid and the hydrogen ion concentration. If *two* of these are kept constant the variation of rate with the third concentration may be studied, *but* it must be remembered that sufficient iodate must be present for the second reaction to occur at all.

Required :

Potassium iodate solution. 10 gm. per litre.

Sodium sulphite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$. 30 gm./litre.

N sulphuric acid.

Starch solution.

The three solutions (which need not be of accurately known strength) are placed in burettes which are suitably labelled. A preliminary titration is then carried out, using 10 c.c. sodium sulphite solution, acidified with a little of the N sulphuric acid, to find the minimum volume of potassium iodate solution needed to liberate iodine (starch indicator). If about 10–20 c.c. of the acid is added, after diluting the sulphite, sulphur dioxide will not be liberated and the titration can be carried out in the ordinary way. About 10 to 15 c.c. of potassium iodate will be required.

(a) In the first experiments a fixed volume of potassium iodate, which is 2 or 3 c.c. over the minimum quantity ascertained above, will be sufficient (15 c.c. probably will be suitable). This volume may be called x c.c. The variation of the time of reaction with the acid concentration is then studied. x c.c. of potassium iodate is run into a measuring cylinder and diluted to 200 c.c. In another measuring cylinder 10 c.c. of sodium sulphite are diluted with 100 c.c. of water, then 5 c.c. of N acid are added and the volume is made up to 200 c.c. with water. This solution is then placed in a large beaker and a little starch solution is added. On pouring in the iodate solution a stop watch is set going. A dark blue colour appears suddenly after about 2 minutes (at 18°). In successive experiments more acid is present, and the time for the experiment is reduced to only a few seconds:

c.c. Na_2SO_3	c.c. KIO_3	c.c. H_2SO_4	Total.	Time.
10	x	5	400	
10	x	10	400	
10	x	15	400	
10	x	20	400	
10	x	25	400	
10	x	30	400	
		(n)		(t)

The values of $1/t$ and n should be plotted on a graph. An excellent straight line relationship should be obtained.

(b) Having ascertained the concentration of sulphuric acid which gives a period of about 30 or 40 seconds, the effect of increasing the concentration of iodate may be studied. Suggested quantities are:

c.c. Na_2SO_3	c.c. KIO_3	c.c. H_2SO_4	Total.	Time.
10	x	20	400	
10	$2x$	20	400	
10	$3x$	20	400	
10	$4x$	20	400	
	(N)			(t)

As before, a graph may be drawn, plotting $1/t$ and N .

Experiments on the Distribution Law

When a solute distributes itself between two immiscible solvents which are in contact, and the solute has the same molecular condition in each solvent, it follows from the Phase Rule that

$$\frac{c_1}{c_2} = K \text{ (the distribution coefficient).}$$

For this law to hold, even approximately, over a fair range of concentrations, the solutions must all be very dilute.

(1) Distribution of Succinic Acid between Water and Ether.

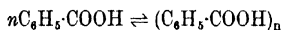
Two solutions of succinic acid are required: one of 5 gm. in 250 c.c. of water and the other of 5 gm. in 500 c.c. of water. 50 c.c. of each of these are placed in each of two stoppered bottles which are kept standing in water at room temperature. To each, 50 c.c. of ether are added and the mixtures are shaken at intervals for half an hour. The two layers are then separated with a separating funnel and in each case titrated with $\frac{N}{10}$ alkali, using phenolphthalein indicator. The ether solutions are titrated in glass-stoppered bottles with frequent shaking. The volumes of alkali (v_1 and v_2) used for the two layers are proportional to the concentrations of acid in the layers. The ratio v_1/v_2 should be found to be very nearly the same for the two experiments.

(2) **The Distribution of Benzoic Acid between Water and Benzene.** Solutions of 0.5, 0.7 and 1.0 gm. of benzoic acid in 100 c.c. of benzene (sp. gr. 0.88) are needed. As in experiment (1) these are shaken with an equal volume of water for about half an hour. The two layers are then separated and 10 c.c. portions of the benzene layer are in each case titrated with $\frac{N}{50}$ alkali using phenolphthalein. A small glass-stoppered bottle is needed. The aqueous layers are titrated in 25 c.c. portions. Hence the volumes v_1 and v_2 of $\frac{N}{50}$ alkali needed for the whole layer are calculated in each case. It will be found that in this case

$$\frac{v_1}{\sqrt{v_2}} = \text{constant}$$

where v_2 refers to the benzene layer and v_1 to water.

The explanation is that benzoic acid is largely associated in benzene:



By applying the law of Mass Action it may be shown that when the degree of association is nearly 1.0

$$\frac{c_1}{n\sqrt{c_2}} = \text{constant}$$

(3) The distribution of Iodine between Water and Benzene.
Evidence for the complex ion I_3^- .

Required :

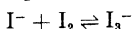
- " $\frac{N}{10}$ potassium iodide (accurately known).
 $\frac{N}{10}$ sodium thiosulphate (accurately known).
 $\frac{N}{100}$ sodium thiosulphate (accurately known).

Iodine.

Benzene.

The distribution coefficient for iodine in water and benzene can be found by shaking 0.5 gm. of iodine with 100 c.c. of water and 25 c.c. of benzene for half an hour. The layers are then separated and 5 c.c. portions of the benzene layer and 50 c.c. portions of the aqueous layer are titrated against $\frac{N}{10}$ and $\frac{N}{100}$ thiosulphate respectively, using starch indicator.* The result may be checked by repeating the experiment, but using 1 gm. iodine in place of 0.5 gm.

To verify the formula I_3^- for the complex ion formed by iodine in potassium iodide solution the above experiment is repeated, using $\frac{N}{10}$ potassium iodide in place of water in the two cases. If in each case c_1 represents the concentration in the benzene layer, the concentration c_2 in water of molecular iodine can be calculated from the distribution coefficient. If c_2' is the concentration in the potassium iodide layer, the difference, $c_2' - c_2$ represents the amount of iodine used up in forming a complex ion. All these concentrations must be expressed in gram-molecules per litre (molarities). If we assume the formation of the complex ion to be correctly represented by



we have, for the equilibrium constant :

$$\frac{[I_3^-]}{[I^-][I_2]} = K$$

* Notes. The 5 c.c. pipette must not be used in the mouth, but is attached to a filter pump which is only slightly turned on. The titration of this benzene solution against thiosulphate must be done very slowly and with continued shaking. The dark colour of the benzene solution goes at the end point. If starch solution is used it will be found that the blue colour goes at each addition of thiosulphate and returns on shaking.

For titrating the aqueous layer $\frac{N}{100}$ thiosulphate is really essential since the titre, using $\frac{N}{10}$ solution, is less than 1 c.c.

To show that this expression does, in fact, give a constant, at least two separate experiments are necessary. Using $\frac{N}{10}$ potassium iodide as before, therefore, the distribution of iodine is again studied, this time using 1 gm. of iodine, 25 c.c. of benzene and 100 c.c. of potassium iodide solution. A second series of values for c_1 , and c_2' is then obtained. As before, the value of c_2 is calculated from the distribution coefficient.

In calculating the value of the equilibrium constant in the two experiments we have, for the molarities:

$$\begin{aligned} [I_2] & c_2 \text{ gm.-mols. per litre.} \\ [I_3^-] & c_2' - c_2 \text{ gm.-ions per litre.} \\ [I^-] & \frac{1}{10} - (c_2' - c_2) \text{ gm.-ions per litre.} \end{aligned}$$

Whence :

$$\frac{(c_2' - c_2)}{(\frac{1}{10} - c_2' + c_2)c_2} = K$$

INORGANIC PREPARATIONS

The preparation of oxides and salts by the ordinary general methods has been indicated on page 1. In making a selection of preparations by methods employing less familiar reactions, only those preparations which yield products in a good state of purity and which do not require an excessive time for their performance have been included. Some of the preparations may be regarded as alternatives to others, but so far as is possible the student should familiarise himself with every preparation described. Many are of interest because they—or the substance formed—illustrate some theoretical point.

Preparations must be regarded as more or less a waste of time and material if the chemistry of the whole process is not clearly understood *in advance*. For this reason the notes to the sections and the equations given before each preparation should be studied. Much time is saved if the parts of apparatus frequently wanted are kept together. After use apparatus should be thoroughly cleaned. Quantities of materials used need be weighed only roughly on a sheet of paper, counterpoising with a similar sheet. For more than 20 gm. quantities a spring balance is useful; liquids may be weighed in a beaker or flask. Whenever practicable, however, liquid quantities are given by volume.

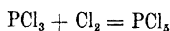
It should be regarded as of the first importance to preserve a good specimen of a preparation. Ordinary specimen tubes fitted with corks are satisfactory for solids which can be exposed to air. In other cases the specimens should be sealed. A soft glass test tube should be heated at its mid-point in a hot flame and, when thoroughly soft, withdrawn and drawn out carefully to produce a constriction one or two inches in length. When properly made such a tube is both easily filled and easily sealed with the Bunsen flame.

SECTION 1. HALIDES

The halides of the elements include typical electrovalent salts such as the alkali halides, and typical covalent compounds such as the sulphur and phosphorus halides. Intermediate in character are such halides as arsenic and antimony trichlorides which exhibit both characters to some degree.

It will be noted that the reactions of certain halides indicate an expansion of the outer shell of electrons beyond the octet which is characteristic of the typical elements.

E.g.



Sidgwick has discussed this question of the covalency maxima of the elements (Speakman, *Valency*, Chap. XI), and shown that it may be regarded as a property of the period of the Periodic Table in which the

element occurs. The general conclusion is that for elements in the second short and first long periods the maximum covalency is 6, and for the remaining elements it is 8.

Some instances are well known, in which an element consistently exhibits a valency which is lower than the maximum associated with its Periodic group. The tervalence of bismuth is an example. This is attributed to a peculiar inertness of a lone pair of electrons which for practical purposes seem, in bismuth, to have become part of the underlying electronic structure or core. It will be found, on examining the problem more closely, that the inert pair (e.g. of Pb and Bi) belongs to a different sub-group (6s) from the ionised electrons which occupy the 6p sub-group. Speakman's *Valency and Modern Atomic Theory* may be consulted.

In view of the impossibility any longer of dismissing the valency of an element by a mere number, it will be necessary to refer to the core or arrangement of electrons beneath the valency group. For a fuller account of the conditions affecting the valency exhibited by an element theoretical works must be consulted. It may simply be remarked here that variable valency may be ascribed to any of the following factors:

- (a) Utilisation of a lone pair in co-ordination, e.g. NH_3 and $[\text{NH}_4]^+$.
- (b) Accepting a lone pair in co-ordination, e.g. AlCl_3 and $[\text{AlCl}_4]^-$.
- (c) Utilisation of a lone pair in forming two covalencies, e.g. PCl_3 and PCl_5 (expansion of the octet).
- (d) Electrons withdrawn from or absorbed into the core,
 e.g. Fe^{++} which has the core 2, 8, 14, (2)
 Fe^{+++} which has the core 2, 8, 13, (3)
 in which the valency electrons are shown in brackets. This is characteristic of "transitional elements."

Anhydrous Aluminium Chloride.

A number of anhydrous metallic chlorides may be made by heating the metal in chlorine: AlCl_3 , SnCl_4 , FeCl_3 , CrCl_3 , MgCl_2 , or in HCl gas: SnCl_2 , FeCl_2 , MgCl_2 . Of these the chlorides of magnesium and chromium are not sufficiently volatile to be driven out of a combustion tube by heating.

Required:

A supply of dry chlorine.

About 25 gm. coarse aluminium powder.

The apparatus shown in Fig. 29 consists of a wide combustion tube heated by a combustion furnace. The tube protrudes at one end into

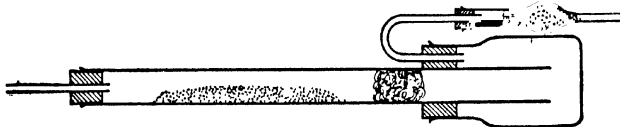


FIG. 29.

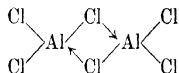
a wide-necked bottle, but this unheated length must be as short as possible since the chloride is to be sublimed into the bottle. A calcium chloride exit tube must be fitted and the experiment is done in the fume chamber. Alternatively, a tube is led from the exit tube out of the window so as to take away the excess chlorine. The aluminium powder is placed in the tube in an even layer and a plug of glass wool or asbestos is used to prevent the powder being carried into the bottle by the gas stream.

All air must be displaced by the chlorine before heating is commenced. Heating then should be gradual at first and finally sufficiently strong to cause the chloride to sublime over (at 183° C.). The reaction is exothermic. When the metal has been converted into the chloride or sufficient chloride has been collected a slow stream of gas is continued while the tube cools. The product is then immediately sealed up in a glass tube or placed in a well-stoppered bottle.

Test.

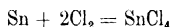
Make a little aqueous solution of aluminium chloride. Test the solution with litmus paper: there is extensive hydrolysis with the formation of colloidal aluminium hydroxide. Add litmus solution and then make the solution alkaline by adding ammonium chloride and hydroxide. The aluminium hydroxide carries down the litmus as a "lake," leaving a clear solution.

Note. Aluminium chloride is soluble in many organic solvents, i.e. it is a covalent compound. In the vapour state it is dimeric: Al_2Cl_6 . This is attributed to co-ordination:



Cf. AuBr_3 , FeCl_3 . The anhydrous chloride readily absorbs ammonia and the compound $\text{H}_3\text{N} \rightarrow \text{AlCl}_3$ can be distilled above 400° C.

Stannic Chloride.



Required:

10 to 20 gm. tin (granulated or foil), supply of dry chlorine.

The apparatus (Fig. 30) is set up in an efficient fume chamber. A small bolt-head flask (100 c.c.) is a convenient reaction vessel. A reflux condenser and delivery tube for chlorine are inserted through the cork, which may be waxed. All the apparatus must be clean and dry.

The tin is placed in the reaction vessel and chlorine (dried by bubbling through concentrated sulphuric acid) is passed in. The excess escapes up the condenser. After a few minutes the tin begins to melt under the heat of the reaction. It is some time, however, before a visible quantity of the liquid chloride is formed. It is unnecessary to heat; it may be desirable to cool the flask in a beaker of water since the chloride boils at

114° C. The chlorine stream must be maintained for a considerable time if all the tin is to be converted into chloride.

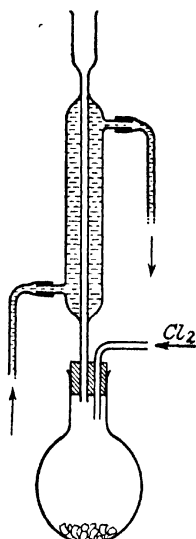
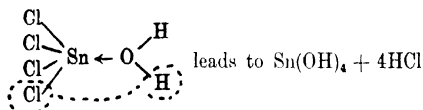


FIG. 30.

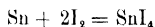
Redistillation of the stannic chloride is inconvenient on account of the dense fumes produced immediately the reaction vessel is opened. It will usually suffice to seal up the liquid product in a stout glass tube prepared in advance. The substance is used as a smoke in chemical warfare, and the vapour should be avoided.

Note. The ready hydrolysis of this compound is in contrast with the stability of carbon tetrachloride in water. This is attributed to the fact that the covalency maximum for carbon is 4, whereas for tin it is 8:



The carbon atom appears not to be open to attack in this way.

Stannic Iodide.



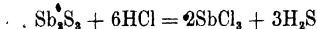
Required:

- 100 c.c. dry carbon tetrachloride.
- 6 gm. iodine.
- 1.3 gm. tin.

Carbon tetrachloride from the bottle must be thoroughly dried by standing overnight in a stoppered flask with anhydrous calcium chloride. 100 c.c. of this are measured into a 250 c.c. round-bottomed flask fitted with a reflux condenser and heated on the water bath. The iodine and tin are added and the mixture heated until no further change can be observed (about 1 hour). The solution is then decanted from any unchanged tin into a distilling flask. The volume of the solution is then reduced to about one-half by distilling off carbon tetrachloride on the water bath. Crystals of stannic iodide separate on standing and may be filtered off. They should be washed with a little cold dry carbon tetrachloride. The red solid melts at 144° C.

Dry chloroform or alcohol (dried over anhydrous sodium sulphate) may be substituted for carbon tetrachloride in this preparation. The experiment is essentially an alternative to the preceding one. Stannic iodide, although a solid, is a covalent compound and is soluble in organic solvents. It is hydrolysed in water.

Antimony Trichloride and Oxychloride.



Required :

50 gm. powdered antimony sulphide (stibnite).

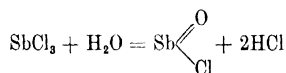
Concentrated hydrochloric acid.

In the direct method of making antimony trichloride by passing chlorine over antimony (at the ordinary temperature) some antimony pentachloride is also formed. The compound is more conveniently made from the natural sulphide.

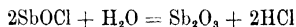
The powdered stibnite is heated with 200 c.c. of concentrated hydrochloric acid in a litre flask placed on a water bath or sand bath. This process must be carried out in a fume chamber since hydrogen sulphide is evolved. The mixture must be shaken at intervals until nearly all the solid has disappeared. The hot solution is then filtered through some glass wool into a large evaporating basin. Evaporation on the water bath is continued (in the fume chamber) until the volume has been reduced to about one-third. On allowing the solution to cool a little lead chloride may separate. The solution, which is usually yellow owing to the presence of ferric salts, is then decanted into a clean dry retort fitted with a 360° C. thermometer and containing a few pieces of broken earthenware.

On distilling, the solution hydrochloric acid comes over first, then a mixed distillate of the acid with antimony trichloride and finally the trichloride alone (b.p. 230° C.). Three or four clean dry flasks are used as receivers to collect these separate fractions. The trichloride can be recognised from the boiling point and the fact that it solidifies in the receiver (m.p. 72°). On account of its appearance it was at one time called "butter of antimony."

On pouring the middle portions of the distillate into a large volume of water the oxychloride may be prepared. It may be washed by decantation and dried on a porous plate in a desiccator.



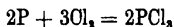
A little oxide may be present in the specimen :



Tests.

1. Dissolve a little antimony trichloride in a solution of tartaric acid or sodium hydrogen tartrate. On diluting with water no precipitate of oxychloride is obtained since the complex salt is stable.

2. On adding caustic soda to a solution of the trichloride in dilute hydrochloric acid a white precipitate of the hydroxide is first formed, but this redissolves in excess alkali, showing that the hydroxide is amphoteric.

Phosphorus Trichloride.

Required :

10 gm. yellow phosphorus.

Supply of dry chlorine.

N.B.—A sand bucket should be available in case of fire through breakage of apparatus.

The apparatus shown in Fig. 31 must be clean and dry, and it should be set up in a fume chamber. Alternatively a lead from the calcium chloride exit tube must be taken out of the window. The chlorine used in the experiment must be washed by passing it through a wash bottle of water and then dried by passing through two bottles of sulphuric acid. A little sand is placed in the retort to prevent excessive local heating. The air in the apparatus should be displaced by a stream of carbon dioxide.

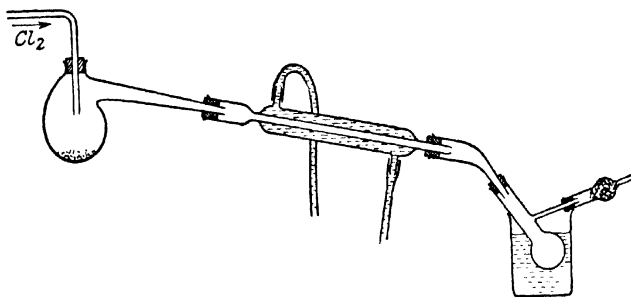


FIG. 31.

Phosphorus may be weighed in a small beaker containing a little water and already counterpoised. It should be cut under water into small pieces which will pass through the neck of the retort. These are dried by gentle pressure between several thicknesses of filter paper before being dropped in. The phosphorus is on no account touched with the fingers.

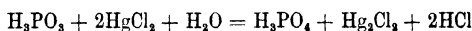
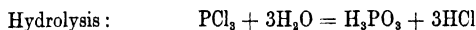
Before commencing to pass chlorine it must be noted that the delivery tube should end near the middle of the retort. If it is too high phosphorus pentachloride will condense as a crust in the neck and tubulus; if it is too low phosphorus is vaporised in the flame of burning chlorine and condenses as a yellow-brown deposit on the sides.

The phosphorus catches fire immediately the chlorine is passed or on gentle warming, but it is usually the chlorine which forms a flame in the phosphorus vapour after a few minutes. Oily drops of the trichloride collect in the receiver. When no more comes over the product is redistilled with a Liebig condenser which is ready to be attached to the arm of the receiver. Phosphorus trichloride comes over between 70° and 80°.

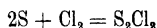
The pure liquid boils at 75° C. It fumes strongly in air and must be sealed up.

Test.

Add a few drops of phosphorus trichloride to about 50 c.c. of water in a beaker. The progress of the hydrolysis can be easily followed. When it is complete the solution should be tested for the presence of chloride ion. The reducing action on mercuric chloride solution should also be noted :



Sulphur Monochloride.



Required :

30 gm. flowers of sulphur or powdered roll sulphur.

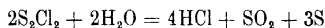
Supply of dry chlorine.

The reaction of sulphur with chlorine produces the monochloride S_2Cl_2 and some dichloride SCl_2 . The sulphur is kept molten in a retort. Except for the condenser, which is omitted, the apparatus is the same as that for phosphorus trichloride. The chlorine must be dried by passing through sulphuric acid.

The sulphur in the retort is not heated until the air in the apparatus has been displaced by chlorine. The bottom of the retort is then evenly heated with a naked flame, especial care being taken until the sulphur is all molten. The reaction is not vigorous and the red distillate collects slowly in the cooled receiver. When enough has been collected a gram or two of sulphur is added and the small distilling flask is fitted with a thermometer (360° range) and an air condenser, so that the product can be distilled. The monochloride distils over between 135° and 140° C., the dichloride being largely reduced by the excess sulphur. The distillate is amber coloured and fumes in air. It must be sealed up in a glass specimen tube.

Test.

A few drops of the monochloride are added to about 20 c.c. of water in a boiling tube. The hydrolysis is hastened by warming, and when complete, chloride ion may be shown to be present.



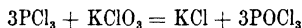
The reaction with caustic soda solution is rapid. The evidence indicates that the compound has the formula :



Phosphorus Oxychloride.*

This compound and the two following compounds are included in this section, although they might have been classified separately as acid

chlorides. They are covalent compounds in which the chlorine atoms are attached to an atom which is also attached to oxygen.



Required :

12 gm. potassium chlorate.

25 c.c. phosphorus trichloride.

A 250 c.c. distilling flask is fitted with a dropping funnel and the side arm is connected with a filter flask fitted with a calcium chloride exit tube. The filter flask, which serves as a receiver, is cooled by cold water. All the apparatus must be thoroughly dry.

The finely powdered potassium chlorate is placed in the flask and the phosphorus trichloride run in drop by drop from the dropping funnel. It may be necessary to heat the flask gently to start the reaction, but once started heat is evolved and some phosphorus trichloride may distil over into the receiver (b.p. 75°C). If this happens it should be returned to the dropping funnel.

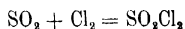
When all the trichloride has been added the flask is heated evenly with a Bunsen flame. The dropping funnel is replaced by a thermometer and the fraction boiling between 106° and 110° is collected separately. The pure oxychloride boils at 108°C . It fumes in air and must be sealed up in a glass tube.

Test.

On adding a little of the oxychloride to water hydrolysis takes place



Sulphuryl Chloride.



Required :

50 gm. camphor.

Supply of dry chlorine.

Supply of dry sulphur dioxide.

The two gases combine in the presence of a catalyst, which may be either camphor or active charcoal. The camphor, used here, is placed in the flask A shown in Fig. 32.

To begin with the water bath contains cold water. Sulphur dioxide is led into the apparatus for about ten minutes, and this is largely absorbed by the camphor. When a supply of chlorine is used in place of the sulphur dioxide the reaction commences and a little liquid collects in the flask A. Both gases may now be admitted together and at about equal rate. Some sulphuryl chloride may distil over into the receiver. When sufficient has been formed it is all distilled over by raising the temperature of the water in the water bath.

The crude product which is collected needs to be redistilled. The receiver is accordingly fitted with a thermometer and a condenser. The distillate, which comes over between 65° and 72° , is collected and sealed

up. The compound fumes very strongly in air, and it is very desirable that it should always be handled in the fume chamber.

The camphor should be preserved for another occasion in a well-stoppered bottle.

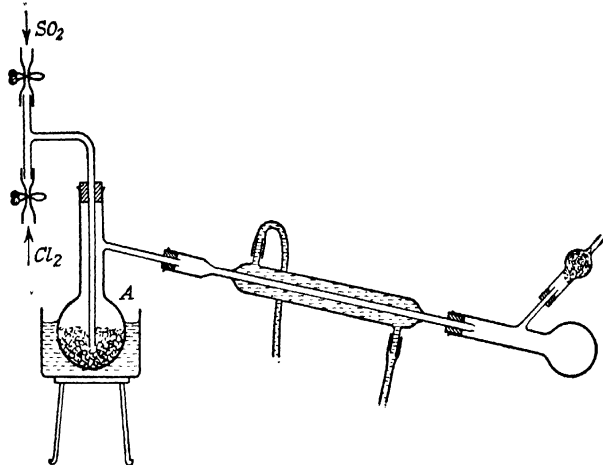
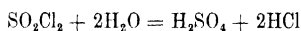


FIG. 32.

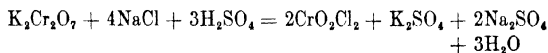
Test.

A few drops of sulphuryl chloride, added to cold water, undergo rapid hydrolysis. The solution should be tested for the presence of both sulphate and chloride ions.



Chromyl Chloride.

This compound is exactly analogous to the preceding one and bears the same relation to chromic acid H_2CrO_4 as sulphuryl chloride does to sulphuric acid.



Required :

- 25 gm. sodium chloride.
- 30 gm. potassium dichromate.
- 40 c.c. concentrated sulphuric acid.

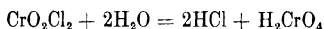
The potassium dichromate and salt are first powdered together in a mortar and then fused on an iron sand tray. When cold the solid mass is returned to the mortar and finely ground. It is then transferred to a medium-sized retort fitted with a dropping funnel and a Liebig condenser. The apparatus must be set up in the fume chamber. The method of

receiving the distillate is as shown in the figure for phosphorus trichloride (p. 140).

The sulphuric acid is placed in the dropping funnel and run very slowly into the retort. Some hydrogen chloride and a little red distillate are formed. When all the acid has been added the retort is carefully heated. Hydrogen chloride and chlorine escape from the exit tube and more red distillate comes over. When no more distillate is seen to be formed the receiver is fitted with a thermometer and connected with the Liebig condenser so that the crude product can be redistilled. The fraction which distils between 112° and 120° should be preserved in a strong glass tube well sealed up. The liquid resembles bromine in appearance. It fumes in air and is hydrolysed by water.

Test.

A few drops of chromyl chloride are allowed to react with 5 or 10 c.c. of water in a test tube. When the heavy oil has disappeared the yellow solution should be tested for the presence of chloride ion.



A little hydrogen peroxide added to the yellow solution gives an intense blue colour due to the formation of "perchromic acid" CrO_5 .

SECTION 2. SALTS.

The preparations given here have been selected on the grounds that (i) the reactions involved are of interest from the theoretical standpoint, and (ii) the salts cannot conveniently be made by the ordinary general methods.

Potassium Bromate.

Bromic acid, HBrO_3 , is known only in solution. The sodium and potassium salts are readily made by the action of bromine on caustic alkali.



Required :

56 gm. potassium hydroxide.

20 c.c. bromine.

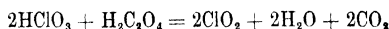
The caustic potash is dissolved in 250 c.c. of water in a 500 c.c. flask heated by hot water to 75°C . The apparatus should be set up in the fume chamber, and the bromine is placed in a dropping funnel held in a stand so that it can be added drop by drop to the alkali. When all the bromine has been added the solution is transferred to a beaker or crystallising dish and allowed to cool. Potassium bromate is much less soluble than the bromide, which is also formed and crystallises out in the form of hexagonal crystals. After 24 hours these are separated and recrystallised from about 100 c.c. of boiling water.

The potassium bromide left in the mother liquors from the preparation is not wasted but obtained by evaporating to dryness. By gentle ignition

the bromate present is decomposed to bromide. Recrystallisation from a little hot water gives a purer product.

Test.

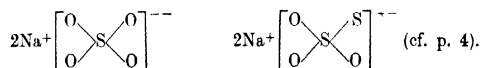
On gently heating a very small quantity of potassium bromate with an equal amount of crystalline oxalic acid in a test tube, a violent reaction takes place. Bromine and hydrogen bromide are among the products. If the experiment is performed with potassium chlorate the yellow gas chlorine dioxide is formed :



Bromine dioxide cannot be made by an analogous method.

Sodium Thiosulphate.

The oxidation of sodium sulphite to sodium thiosulphate is exactly parallel to the oxidation to sulphate. The relation of the sulphate and thiosulphate is :

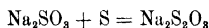


Required :

30 gm. sodium sulphite $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$.

10 gm. flowers of sulphur.

The sulphite is dissolved in 200 c.c. of water and the solution is heated just below its boiling point with the sulphur. It is essential to stir the mixture frequently. After about one hour the sulphur is mostly taken up by the solution which is no longer alkaline to litmus paper. At this stage the solution is filtered from excess sulphur and concentrated by evaporation to about 30 c.c. The cold solution may require seeding with a crystal of the salt to induce crystallisation. The crystals, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, are then filtered off. If desired, a purer specimen may be made by recrystallisation from 25 c.c. of hot water.



Tests.

1. A little silver chloride may be made by mixing silver nitrate and sodium chloride solutions. After decanting the solution from the precipitate it will be found that an excess of sodium thiosulphate solution will dissolve the silver chloride. The formula $\text{Na}_3[\text{Ag}_3(\text{S}_2\text{O}_3)_4] \cdot 2\text{H}_2\text{O}$ has been given to one of the soluble complex salts formed.

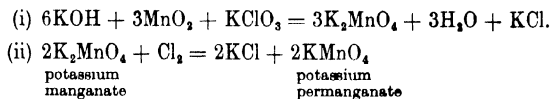
2. If one or two drops of bench hydrochloric acid are added to a little sodium thiosulphate solution a milky precipitate of sulphur is formed after a short delay.

If this test is repeated and one or two drops of methylene blue solution are added immediately after the bench acid the dye is decolorised, presumably by the acid $\text{H}_2\text{S}_2\text{O}_3$ which cannot be isolated. Sulphurous acid will not decolorise methylene blue.

Potassium Permanganate.

In this preparation the oxide MnO_2 is converted into a compound which is a derivative of the oxide Mn_2O_7 . The basic character of the dioxide is weak; it is entirely lacking in the heptoxide, which is purely acidic. The change in valency here is due to the coming into play of the electrons in the $3d$ orbit. The fact that this is readily reversed accounts for the powerful oxidising action of potassium permanganate.

The oxidation is carried out in two stages:



Required:

- 20 gm. potassium hydroxide.
- 10 gm. potassium chlorate.
- 25 gm. manganese dioxide (pyrolusite).

The potassium hydroxide and potassium chlorate are first melted together on a sand-tray or in a fireclay crucible. The manganese dioxide is then stirred in without further heating until all has been added. Heat is produced by the reaction of the acidic oxide and the molten alkali, and the melting point of the mixture rises. When all the manganese dioxide has been added the mass is heated to dull redness for ten minutes. A dark green mass of potassium manganate is obtained (first equation).

When the mass is cool the iron tray is hammered underneath to loosen the solid, which is then chipped off. It is powdered in a mortar and then boiled with 300 or 400 c.c. of water. This extracts the manganate from the residue of unchanged manganese dioxide. The mixture must be well stirred to prevent bumping. The hot solution is next filtered through some glass wool packed fairly tightly in a large funnel and a little hot water may be used to extract the soluble material in the sediment.

The solution is then placed in a large flask and heated on a sand-tray in the fume chamber, while a slow stream of chlorine is bubbled through it. This oxidises the manganate to permanganate (second equation). If preferred carbon dioxide may be used in place of chlorine since manganates are stable only in alkaline solution:



In this case the solution must finally be filtered again. In either case a dark purple solution of potassium permanganate is obtained and this must be slowly evaporated in a large evaporating basin on the water bath until only 20 to 30 c.c. of solution remain. Fine needles of the salt form on standing. These are drained on a porous plate and not filtered on filter paper, since the paper causes reduction of the compound.

Tests.

1. If concentrated sulphuric acid is added drop by drop to a little potassium permanganate in a beaker a dark green solution is formed in

the cold. On warming very slightly a dark purple vapour (Mn_2O_7) is produced, but this almost immediately decomposes violently and a cloud of manganese dioxide is formed. The oxide Mn_2O_7 is the anhydride of permanganic acid.

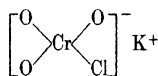
2. The powerful oxidising properties of potassium permanganate may be demonstrated by adding one or two drops of glycerol to a little of the solid on a white tile. After a few moments the glycerol is ignited brilliantly.

Potassium Chlorochromate.

The relation of this salt with chromyl chloride is shown by the formulae. The free acid is unknown.



chromyl
chloride



potassium
chlorochromate

Required :

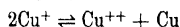
10 gm. potassium dichromate.
Concentrated hydrochloric acid.



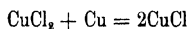
The potassium dichromate is ground to a fine powder and placed in a porcelain evaporating basin. About 10 c.c. of concentrated hydrochloric acid is then added, and the mixture is heated over a small flame to about 60° . A thermometer is used as a stirrer. More hydrochloric acid is added at intervals until a clear dark red solution is obtained. The solution is then covered with a watch glass and left to crystallise for 24 hours. Dark red crystals of the salt separate, and are best drained on a porous plate. The solid cannot be washed with water (owing to hydrolysis) or with alcohol (which would be oxidised). The crystals are finally sealed up in a glass tube.

Cuprous Chloride.

Cupric salts may be reduced to the cuprous condition, but soluble cuprous salts change back rapidly in water :



The cuprous condition is stabilised by the formation of complex ions $[\text{CuCl}_2]^-$ and $[\text{CuCl}_3]^{--}$. Cuprous chloride is soluble in concentrated hydrochloric acid, but sparingly soluble in water.



Required :

10 gm. cupric chloride.
15 gm. copper turnings.
 $1\frac{1}{2}$ litres of boiled distilled water.

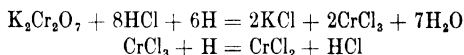
The cupric chloride is dissolved in 250 c.c. of concentrated hydrochloric acid by warming. The copper turnings are added and the mixture

boiled gently for about quarter of an hour in the fume chamber. The hot solution is then decanted into a litre of cold boiled distilled water contained in a tall measuring cylinder. A few crystals of sodium sulphite may be dissolved in this water before the cuprous chloride solution is added, since this hinders oxidation. A white precipitate of cuprous chloride is formed. This is washed by decantation with some more boiled water (containing a little sulphite and acidified slightly). Finally, the precipitate is washed on the filter at the pump, using for this purpose a little alcohol. It is then quickly transferred to a porous plate which is placed in a desiccator containing concentrated sulphuric acid. It must be kept in a well-stoppered bottle.

Chromous Acetate.

The valency of chromium in potassium dichromate is 6; this (maximum) valency depends on the employment of 3*d*. electrons. The chromous ion is divalent. Chromous salts are in general blue; chromous acetate is exceptional in being red.

The reduction takes place in two stages:

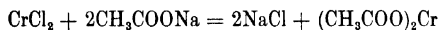


(this formulation rests on the assumption that reduction is due to nascent hydrogen).

Required:

- 25 gm. potassium dichromate.
- 40 gm. granulated zinc.
- 150 c.c. concentrated hydrochloric acid.
- 50 gm. sodium acetate.
- 200 c.c. cold boiled water.

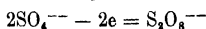
The potassium dichromate and zinc are placed in a litre flask, which is fitted with a dropping funnel and a delivery tube which dips below the surface of some water in a beaker. The entry of air is thus prevented. Through the funnel a mixture of 100 c.c. of water and 150 c.c. concentrated hydrochloric acid is added *gradually*. A vigorous reaction takes place, hydrogen is evolved and the dark green colour of the Cr^{+++} ion is seen before giving place to the blue colour of the Cr^{++} ion. When the reaction is over and the solution is blue it is poured quickly through a Buchner filter into a solution of 50 gm. sodium acetate in 350 c.c. of water. Double decomposition takes place:



The red acetate is precipitated. This is filtered off at the pump and washed with cold boiled water. It is drained on a porous plate and quickly bottled in the moist condition. The compound is oxidised quite rapidly in air. Other chromous salts can conveniently be made from the acetate.

Potassium Persulphate.

In electrolysis of a solution containing SO_4^{--} ions, e.g. sodium sulphate or sulphuric acid, the electrode potential necessary for the discharge of these ions is not usually reached. Instead OH^- from the water are discharged. Using a sufficiently high current density it is possible to bring about anodic oxidation of the sulphate ions:



Required:

Sulphuric acid sp. gr. 1.3 (51 gm. of concentrated sulphuric acid in 100 c.c. of solution).

Potassium sulphate.

The electrolysis cell shown in the figure should be set up. The cathode consists of platinum wire wound on a piece of wide glass tubing. Through the cork passes a piece of ordinary glass tube, into the closed end of which is a short piece of platinum wire. This should project about 1 cm. Contact with the anode is made through a little mercury. The large beaker contains ice and water.

Enough sulphuric acid to fill the boiling tube is saturated with potassium sulphate at between 0° and 5°C . This solution is the electrolyte. A six-volt supply is then connected with the electrodes, an ammeter being included in the circuit. A current density of about 1 amp. per square cm. is needed and if a rough calculation shows that this is not attained the current must be increased suitably.

Shortly after switching on the current small crystals of potassium persulphate begin to separate at the bottom of the tube. After about half an hour there should be enough of the solid to collect on a porous plate. Potassium persulphate is only sparingly soluble. The crystals should be washed with a little alcohol and ether and dried on filter paper.

Note. A solution of potassium persulphate gives most of the reactions of a solution of hydrogen peroxide, but it does not decolorise potassium permanganate solution nor does it give a yellow colour with a titanous salt or a blue colour with chromic acid.

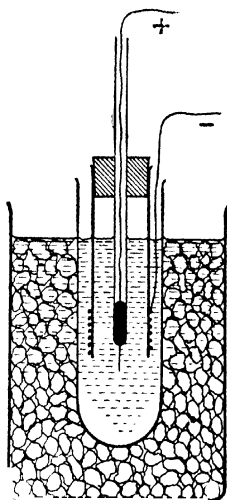


FIG. 33.

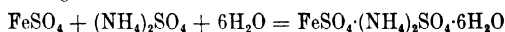
SECTION 3. DOUBLE SALTS AND SALTS CONTAINING • COMPLEX IONS

Double salts conform to the law of constant proportions, but they exist only in the solid state. Their solutions contain the ions of the simple

salts from which they are formed. Complex salts give either anions or cations which are composite and cannot be split up into simpler components without complete loss of identity. Examples of complex ions are :

Anions.	Cations.
$[\text{Fe}(\text{CN})_6]^{---}$	$[\text{Cu}(\text{NH}_3)_4]^{++}$
$[\text{Fe}(\text{CN})_6]^{----}$	$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{++}$
$[\text{SiF}_6]^{--}$	$[\text{Co}(\text{NH}_3)_6]^{+++}$

The successful preparation of double salts depends on the crystallisation of a solution containing the two component salts in the requisite proportions, e.g.

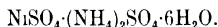


Some complex salts may be made just as simply. The fact that some complex salts are partly dissociated in solution means that there is no sharp distinction between the two classes. Complex ion formation is a property which is well distributed in the Periodic Table, but it is particularly well marked in the so-called "transition elements." The colour associated with the simple ions of these elements is also found in their complex ions, but the colours are not usually the same.

An important feature of complex ion formation is the stabilisation of otherwise unstable valency groups. This is well marked in the case of trivalent cobalt, and monovalent copper salts. The complex salts derived from these are in many cases quite stable.

Nickel Ammonium Sulphate.

This is regarded as a double salt with the formula



The solution has all the properties of the two separate salts, and there does not appear to be any complex ion formation.

Required :

50 c.c. concentrated sulphuric acid.

50 gm. nickel carbonate.

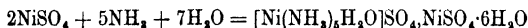
Ammonia solution (sp. gr. 0.88).

The sulphuric acid is first added to 150 c.c. of water, and the dilute solution is divided into two equal parts. One of these is neutralised by the addition of nickel carbonate. About 50 gm. are needed, but a slight excess should be added and the mixture finally warmed. The clear solution is then decanted or filtered at the pump from the excess solid.

The other portion of sulphuric acid is next neutralised by the addition of strong (0.88) ammonia solution. About 60 to 70 c.c. will be required. The two solutions are then mixed and left to crystallise. A few c.c. of dilute sulphuric acid should be added to the mixed solution as this minimises the risk of partial hydrolysis of the nickel salt. The crystals are finally drained and dried between pieces of filter paper. Recrystallisation from a little water acidified with dilute sulphuric acid is necessary to obtain a specimen of the greatest purity.

Pentammino-dinickel Sulphate.

This salt, with the formula $[\text{Ni}(\text{NH}_3)_5\text{H}_2\text{O}]\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is the most easily formed of the nickel amines.



Required :

50 gm. nickel sulphate.

Ammonia solution (sp. gr. 0.88).

Ice.

50 gm. of nickel sulphate are dissolved in 50 c.c. of water by warming. The solution is cooled quickly to 5° or 10° by surrounding it with ice and water and then, before crystallisation commences, 100 c.c. of strong ammonia solution are added in small portions, the mixture being shaken and kept cool. The solution goes a dark violet colour, but the violet precipitate formed by the ammonia as it runs in, redissolves on shaking. To obtain the solid complex salt 50 c.c. of industrial alcohol are floated on the surface of the solution with the help of a pipette. On standing overnight a quantity of the violet crystals separate and can be filtered at the pump. The solid is washed with a little dilute alcohol and dried on a porous plate or between pieces of filter paper.

Chrome Alum.

The alums are double salts containing a great deal of water of crystallisation, which appears to be held only loosely in the crystal lattice. The general formula is $\text{M}_2\text{SO}_4 \cdot \text{M}_2'(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

Required :

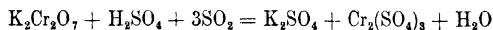
25 gm. potassium dichromate.

15 c.c. concentrated sulphuric acid.

A supply of sulphur dioxide.

Ice.

This double salt may be made by crystallising a solution containing equimolecular parts of the two components, K_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3$. It is essential, however, not to heat the chromic sulphate above 70° C. since a non-crystallisable salt with the formula $[\text{CrO}(\text{SO}_4)_4]\text{SO}_4$ is formed. To get a solution of sufficiently great concentration of both salts, therefore, without heating, the reduction of potassium dichromate is the best method :



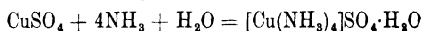
The dichromate is dissolved in 100 c.c. of warm water and then cooled before adding the concentrated sulphuric acid. It must then be cooled below 30° before passing sulphur dioxide, and during the reduction the temperature must be kept below 40°. For this purpose a measuring cylinder standing in an outer vessel containing water is suitable. A slow stream of sulphur dioxide is then passed, the delivery tube reaching nearly to the bottom of the solution.

The reduction is continued until a drop of the solution placed on a

filter paper shows no trace of orange colour. The dark green solution is then placed in a beaker surrounded by a mixture of ice and salt. Scratching the side of the beaker with a freshly cut glass rod may help to induce crystallisation. If no ice is available the solution may be left to stand for several days. The crystals are finally filtered off at the pump and drained on a porous plate or on filter paper. They are dark purple octahedra.

Tetrammino-cupric Sulphate (Cuprammonium Sulphate).

Under the name of cuprammonium sulphate this is one of the best known complex salts. Whereas nickel is able to accommodate up to six molecules of ammonia or certain other univalent groups around the central atom, no complex copper ion is known with more than four. The "coordination number" of copper is therefore four.



Required :

10 gm. copper sulphate crystals.

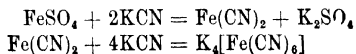
Ammonia solution (sp. gr. 0.88).

The copper sulphate is dissolved in 50 c.c. of water in a conical flask of medium size. Ammonium hydroxide composed of one volume 0.88 ammonia diluted with two volumes of water is then added slowly until, with stirring, the basic copper sulphate first precipitated is redissolved. The dark blue solution contains the complex salt, but this cannot be crystallised by evaporation since the compound would suffer decomposition. It is accordingly thrown out of solution by the addition of alcohol, in which it is only sparingly soluble.

20 c.c. of industrial alcohol are floated on the surface of the solution with the help of a pipette, and the flask is corked and left undisturbed for some hours. As the alcohol diffuses into the solution the cuprammonium sulphate separates in the form of small dark blue crystals. These are filtered at the pump, washed with a little alcohol and dried on filter paper. On exposure to air the crystals slowly lose ammonia.

Potassium Ferrocyanide.

Sparingly soluble ferrous cyanide is soluble in potassium cyanide solution to give the salt potassium ferrocyanide.



Required :

20 gm. pure ferrous sulphate.

30 gm. potassium cyanide.

Note. Potassium cyanide is exceptionally poisonous. The warm aqueous solution liberates hydrogen cyanide, which is an extremely poisonous gas.

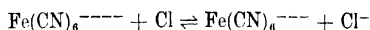
The ferrous sulphate is dissolved in 100 c.c. of cold water by stirring. Heat should not be applied since the ferrous salt is easily oxidised to the

Ferric state: A cold solution of 30 gm. potassium cyanide in 100 c.c. of water is then added. Ferrous cyanide is precipitated but, on boiling in the fume chamber for ten minutes, most of the precipitate dissolves up in the excess cyanide solution. After standing for two or three minutes the clear solution is decanted or filtered and then evaporated to about half its volume. The evaporation should be done in the fume chamber. On standing, the complex salt crystallises. The crystals are separated and then recrystallised from about 25 c.c. of water. They have the formula $K_4Fe(CN)_6 \cdot 3H_2O$.

Tests.

1. On addition of potassium ferrocyanide solution to a solution of a ferric salt a dark blue precipitate of "prussian blue" is formed. If there is excess of ferric salt the precipitate has the formula $Fe_4[Fe(CN)_6]_3$. If there is excess potassium ferrocyanide some "soluble prussian blue" is formed: $KFe[Fe(CN)_6]$.

2. To convert potassium ferrocyanide into potassium ferricyanide chlorine is bubbled through a solution of about 5 gm. of the salt dissolved in 20 c.c. of water.



When the solution no longer gives a blue precipitate with a ferric salt it is evaporated until the ferricyanide begins to crystallise. This has the formula $K_3[Fe(CN)_6]$ and is poisonous. The solution is slightly hydrolysed.

ORGANIC PREPARATIONS

With the compounds of organic chemistry we meet with what are, for the most part, covalent compounds. Le Bel and van't Hoff (1874) first proposed that the valencies of a saturated carbon atom are directed towards the apexes of a regular tetrahedron. This fruitful idea of directed links or bonds explains the interest of the organic chemist in structure and in the possibilities of isomerism. In general there are none of the intensely strong electrical fields due to ions to be found in the close vicinity of the molecules of organic compounds. Reactions between such compounds are accordingly much slower, but it would be a mistake to suppose that the force involved in a covalent link is much less than that involved in an electrovalent compound consisting of two univalent ions (Speakman, *Valency*, Chap. VI). Not only are the reactions of organic chemistry in the main molecular, but they should be thought of as concerning only particular groups or centres, the rest of the molecule being comparatively inert. Organic chemistry would be simply the chemistry of certain characteristic groups such as $-\text{CH}_3$, $-\text{CH}_2\text{OH}$, $>\text{C}=\text{O}$ and the rest, if it were not that the groups have mutual effects on each other. This fact, which has long been known, is receiving considerable theoretical explanation, but the subject is usually studied after the student has gained a good grasp of the more elementary facts.

It has been necessary to make a selection of organic preparations suitable for an introductory course, but enough have been included to cover all the compounds (and their reactions) with which the student can normally be expected to be familiar in the laboratory at this stage.

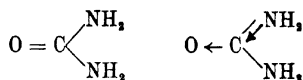
It cannot be too strongly emphasised that a good grasp of the principles employed in studying equilibrium through the law of Mass Action is essential (see p. 6). Many of the reactions are reversible and those which, in the practical sense, are not, proceed at rates which are governed by the ordinary mass law considerations. As Gatterman remarks in his *Laboratory Methods of Organic Chemistry* (1932), a grasp of these theoretical principles "is indispensable to anyone who does not wish to practise organic chemistry merely as a culinary art."

It should be obvious that cleanliness is just as important here as in all branches of chemistry, but there is an unfortunate tradition that organic chemistry is necessarily messy. It is true that greater trouble is frequently met in cleaning apparatus which has been used for an organic preparation, and for this reason suggestions are given in the appendix for the removal of tarry residues. Apparatus should, however, not be left in a dirty condition, and everything that can be done to reduce the time spent in looking for apparatus, pieces of tubing, rubber stoppers, etc., should be done.

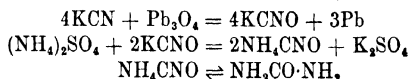
An urgent reminder about the risk of fire may be required. Necessary

precautions are given in the text. Unnecessary danger must arise if bottles of inflammable and volatile compounds are left on benches or in the vicinity of a flame.

Urea.*



The method described here is to convert potassium cyanate into ammonium cyanate. This then undergoes readily the isomeric change into urea (possibly through the intermediate compound isocarbamide):



Required :

50 gm. potassium or sodium cyanide.

140 gm. red lead.

25 gm. ammonium sulphate.

The first step is the oxidation of the cyanide to cyanate. The solid cyanide is melted on an iron sand tray and the red lead is stirred in, small quantities at a time. Heat is evolved and the evolution of oxygen causes some frothing. When all the red lead has been added and a dark liquid melt is obtained, the contents of the iron tray are poured on to a second tray and allowed to cool. During solidification the lead formed by reduction forms a cake at the bottom. The crude cyanate is separated as well as possible, crushed in a mortar and then left to stand for about an hour or more in 200 c.c. of cold water. The solution is then filtered and a solution of 25 gm. of ammonium sulphate in about 75 c.c. of water immediately added.

At this stage ammonium cyanate is formed, but only temporarily. The salt quickly undergoes a rearrangement to urea. At equilibrium more than 90 per cent. of urea is formed, and as urea is less soluble than ammonium cyanate, crystallisation of the solution by evaporating brings about complete conversion. The mixed solutions are accordingly placed in a large evaporating basin and heated on the water bath to dryness. The solid residue consists of urea and potassium sulphate. *When dry* this is transferred to a small flask fitted with a reflux condenser and heated on a water bath. A little animal charcoal is added (2 or 3 gm.) and then three or four successive quantities of about 50 c.c. of industrial alcohol are used to extract the urea. The separate extracts are filtered hot through double filter paper fluted. From the collected filtrate about two-thirds of the alcohol is removed by distillation on the water bath and the remain-

* The first is the ordinary formula. The second is one of two other formulae which can be written. The third is the same as the second, but showing the co-ordinate link on the other N atom. Urea is thought to be a "resonance hybrid" and its correct representation requires all three formulae.

der is left to cool in a beaker. The crystals of urea are then filtered at the pump and dried in the steam oven. Yield about 15 gm. m.p. 132°C .

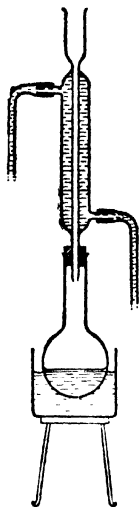


FIG. 34.—Flask fitted with Reflux Condenser.

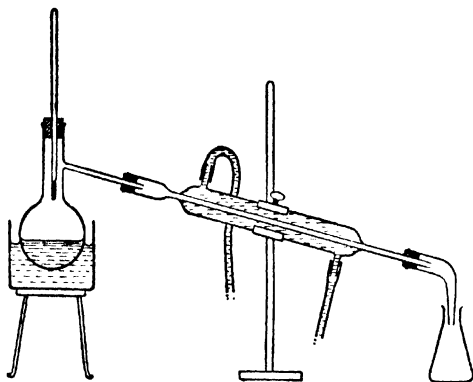


FIG. 35.—Distilling Flask set up for Distillation on the Water Bath.

Note. Urea is the amide of carbamic acid NH_2COOH which, however, is known only in its derivatives. It is also clearly related to phosgene COCl_2 and can be made from this compound by the action of ammonia.

Tests.

1. Like all amides urea gives ammonia when heated with caustic alkali. Warm a little of the solid with some caustic soda solution in a test tube. Ammonia may be recognised readily.

2. On heating a little urea in a clean test tube it first melts and then decomposes, giving ammonia among other products. The solid residue contains biuret, $\text{NH}_2\text{CO-NH-CO-NH}_2$. An aqueous solution of this, mixed with a few drops of copper sulphate solution and then made alkaline with caustic soda, gives a violet or pink coloration. ("Biuret test.")

3. If a little urea is dissolved in dilute nitric acid and then excess of concentrated nitric acid is added, on cooling under the tap urea nitrate separates as a well-crystallised salt.

Determination of the melting point of urea. The melting point of a substance is found by heating it in a short length of capillary tube with very thin walls in a melting-point bath. The latter is best made of some high-boiling-point paraffin heated by a very small flame in a small beaker.

An efficient stirrer must be used. A 360° C. thermometer (preferably checked against a standard thermometer) is held upright in a clamp with its bulb in the melting-point bath (Fig. 36). The stirrer is made of fairly thin glass rod. It is moved slowly up and down while the temperature of the bath is slowly raised.

Melting-point tubes can be bought, but they are very easily made by pulling out a soft glass test tube after it has been thoroughly heated to the softening point. Each melting-point tube should be about 8 cm. long and about 1 mm. in diameter. One end is sealed by holding it in the outer edge of the Bunsen flame.

A little finely powdered urea is shaken down the melting-point tube,

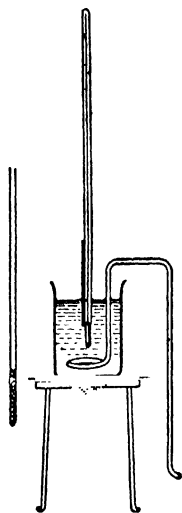


FIG. 36.

which is tapped on the bench so that a firmly packed layer about 1 cm. long is formed at the bottom. The filled tube is then placed up against the side of the thermometer; if a little paraffin is smeared up the side of the thermometer for a few cm. the melting-point tube will adhere by capillary action. The temperature of the melting-point bath is then slowly raised. It is especially important that the rate of rise should be slow over the 5° or 10° before the expected melting-point. The temperature at which the solid liquefies is easily observed if the melting-point tube is in such a position that light is transmitted through it. If necessary a second determination is carried out after the bath has cooled sufficiently. The temperature of solidification of the liquid substance is never used owing to the effect of supercooling.

Mixed melting points. When a substance is already identified a melting-point determination serves as a test of purity since, as a general rule, an impure specimen melts at a lower

temperature than the pure substance. When engaged in *identifying* a substance one frequently finds a mixed melting-point determination of great value. Thus urea melts at 132° C., benzamide $C_6H_5CONH_2$ at 128°. To make sure that a solid, m.p. 128°, is benzamide and not an impure specimen of urea a mixed melting point with (a) benzamide, and then (b) urea, should be performed—the second one only if the result of (a) shows that the substance is not benzamide.

To make a mixed melting-point determination three m.p.-tubes are needed. A is filled with the unknown substance, B with pure benzamide, C with a roughly 50 per cent. mixture of the two. These are mounted side by side and observed together as the temperature is slowly raised. If A and B contain the same substance all three tubes will give the same

melting point, but differing perhaps by 1° if there is a small difference in purity. If A and B contain different substances, even though their m.p.s are practically identical, C will give a much lower m.p. or a gradual liquefying which takes place over a range of temperature. If, in the case mentioned, a mixed melting-point determination gives negative results both for benzamide and urea, the unknown substance must be neither one nor the other. For a specimen of pure urea mixed with an impure specimen the melting point will be intermediate. In such a case it would be highly desirable not to do the mixed m.p. until the impure solid had been recrystallised.

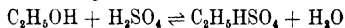
Recrystallisation. If the specimen of urea prepared in the foregoing exercise does not give the expected m.p. but melts at a lower temperature, a purer specimen may be obtained by recrystallisation from a suitable solvent. This process is, in fact, usually carried out with any preparation prior to taking its melting point.

A suitable solvent is first found by performing test tube experiments on very small quantities of the solid. Water, alcohol, glacial acetic acid, benzene and petroleum ether are tried in this order if the best solvent is not known. Acetic acid is not used for basic substances. The minimum amount of solvent which will dissolve the solid near the boiling point is used. On cooling under the tap the solution may deposit crystals, but if this does not occur the side of the test tube is scratched with a glass rod. If the solvent is alcohol or acetic acid the addition of a drop or two of water may assist, and it may subsequently be found that dilute alcohol or acetic acid is the best solvent. Water is never added to solvents with which it does not mix.

When working on a fairly small scale, recrystallisation may be carried out in a conical flask heated on the water bath. The solvent is added a little at a time until there is just sufficient to dissolve the solid at the higher temperature. Fairly rapid cooling is preferred, since this gives small crystals which are readily filtered and dried. The filtrate (or mother liquor) may be distilled to reduce its bulk and recover a further quantity of the substance if it is very soluble. This batch will very probably be less pure.

Potassium Ethyl Sulphate. $\text{C}_2\text{H}_5\text{KSO}_4$.

The ester, ethyl hydrogen sulphate, formed by the action of concentrated sulphuric acid on alcohol, is an oily liquid which is very soluble in water and readily hydrolysed. It is therefore usual to isolate the compound in the form of its potassium salt.



Required :

- 35 gp. (43 c.c.) absolute alcohol.*
- 30 gm. (16 c.c.) concentrated sulphuric acid.
- 25 gm. potassium carbonate.
- 25 gm. chalk.

* Appendix, p. 216.

The alcohol and acid are first mixed in a 250 c.c. round-bottomed flask. Whenever these two liquids are mixed the acid must be added in small quantities to the alcohol, the flask being well shaken during the process. If the addition is too rapid the heat evolved may cause the mixture to boil and at the same time marked darkening of colour due to charring of the alcohol will be observed.

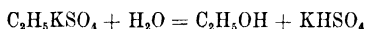
A few pieces of porous earthenware are next added, and the mixture is then heated on a wire gauze, a reflux condenser being fitted so that the heating may be continued without loss of alcohol. The mixture should be maintained at or near its boiling point for about an hour. The liquid contains ethyl hydrogen sulphate, unchanged acid and alcohol. When cooled it is poured into 200 c.c. of cold water in a large basin.

25 gm. of finely powdered chalk are then stirred to a thin paste with water and added very gradually with steady stirring. The excess sulphuric acid is converted to insoluble calcium sulphate. Calcium ethyl sulphate remains in solution. The mixture is then filtered at the pump, using a large Buchner funnel, and the filtrate is returned to the basin. The potassium carbonate, dissolved in water, is then added very carefully until the solution is just alkaline. This converts the calcium salt into the potassium salt and chalk is precipitated. The mixture is again filtered at the pump and the filtrate is evaporated on the water-bath nearly to dryness. The crystals which separate from the cold solution are drained on filter paper and then dried in a desiccator containing calcium chloride. Yield about 20 gm.

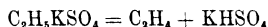
Tests.

1. A little of the salt is dissolved in water and barium chloride solution is added. If the specimen was pure no precipitate of barium sulphate will be formed. Barium ethyl sulphate is soluble.

2. A solution, made as before, is boiled with a few drops of hydrochloric acid. On adding barium chloride there is an immediate heavy ppt. of barium sulphate, showing that the ester is readily hydrolysed :

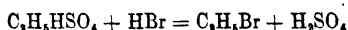


3. A little of the solid is heated in a dry test tube. The inflammable gas ethylene is given off and potassium bisulphate remains :



Ethyl Bromide. $\text{C}_2\text{H}_5\text{Br}$.

This compound may be made by the action of phosphorus tribromide on alcohol or by heating a mixture of alcohol, concentrated sulphuric acid and potassium bromide. In the latter method ethyl hydrogen sulphate is very probably an intermediate product which then reacts with hydrogen bromide :



Required :

32 gm. (40 c.c.) absolute alcohol.

74 gm. (40 c.c.) concentrated sulphuric acid.

50 gm. potassium bromide.

The apparatus required for this preparation consists of a litre distilling flask (or a litre round-bottomed flask fitted with a bent delivery tube), a Liebig condenser, or better, a double surface condenser fitted with an adaptor which dips below the surface of water in a conical flask (Fig. 37). The round flask is heated on a sand bath.

The alcohol and acid are first mixed in the large flask and then cooled to the ordinary temperature under the tap. The potassium bromide, coarsely powdered, is added and the mixture gently heated. Soon ethyl bromide distils over and collects as an oily layer below the water in the

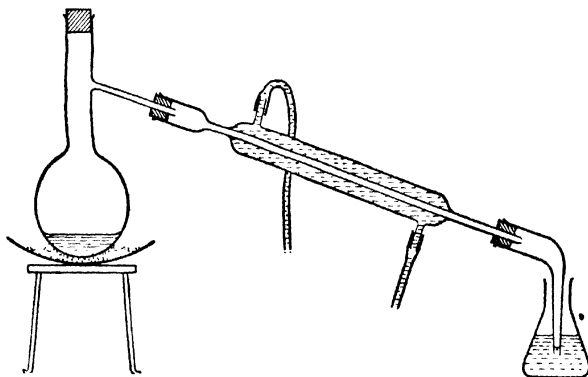


FIG. 37.

receiver. Evaporation of the volatile compound is thus prevented, but it is desirable, nevertheless, to surround the receiver with ice and water. The heating must be moderate, even so the mixture may threaten to froth over, in which case the flask must be quickly raised off the sand bath.

When no more oily drops condense, heating is discontinued and the contents of the receiver are emptied into a separating funnel. The lower layer of ethyl bromide is preserved and the water layer rejected. To remove acid from the bromide it is put back in the funnel and shaken with an equal volume of weak sodium carbonate solution. The funnel is stoppered and held in the inverted position, and the tap is opened frequently to prevent the generation of a dangerous pressure. When no more carbon dioxide is evolved the bottom layer is again preserved and next shaken with an equal volume of water. It is then run into a conical flask containing some fused calcium chloride (2 or 3 gm. should be

M.P.C.

sufficient) and allowed to stand for at least half an hour overnight if this is convenient. The calcium chloride absorbs traces of water and also alcohol.

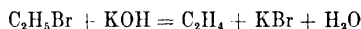
Finally, the bromide, which should be completely clear, is decanted into a clean distilling flask of about 100 c.c. capacity and distilled on the water bath, using an efficient condenser. The distillate, which comes over between 30° and 40°, is preserved in a sealed glass tube. Yield about, 30 to 40 gm., b.p. 38°. Prepared in the above manner it always contains a little ether.

Tests.

1. Add a few drops of the freshly prepared ethyl bromide to some silver nitrate. Very little cloudiness should result, showing that the bromine atom does not ionise.

2. Warm the mixture of ethyl bromide and silver nitrate solution: silver bromide gradually forms owing to hydrolysis. If ethyl bromide is warmed with water the solution becomes acid to litmus.

3. Dissolve a few pellets of caustic potash in about 10 c.c. of alcohol by heating. To the hot solution add 1 or 2 c.c. ethyl bromide. The gas ethylene is evolved. It will burn with a luminous flame in the mouth of the test tube.



Ethyl Iodide. $\text{C}_2\text{H}_5\text{I}$.

Alkyl iodides are rarely made by the action of hydriodic acid on the alcohol. This acid is used in organic chemistry mainly as reducing agent (especially in conjunction with red phosphorus) and for replacing $-\text{OC}_2\text{H}_5$ or $-\text{OCH}_3$ groups by $-\text{OH}$ in aromatic compounds (p. 203). The best method of making ethyl iodide and related compounds is by the action of phosphorus triiodide on the alcohol.



The phosphorus triiodide is formed from the phosphorus and iodine used in the experiment.

Required:

25 gm. iodine.

2.5 gm. red phosphorus.

20 gm. (25 c.c.) absolute alcohol.*

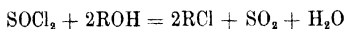
A 250 c.c. round-bottomed flask fitted with an efficient reflux condenser is fitted up as shown in the figure on p. 157. The water bath contains cold water. The phosphorus and alcohol are placed in the flask and the iodine is added in small quantities of about 3 or 4 gm. at a time. Each addition causes the production of heat, but the contents should not boil and the reflux condenser should not be needed at this stage. When all the iodine has been added the mixture is heated on the boiling water bath for about an hour with the reflux condenser in position.

* Ordinary industrial alcohol will not do here. For the preparation of absolute alcohol see Appendix, p. 216.

The condenser is then connected to the flask by a piece of bent tubing, so that the contents can be distilled on the water bath. Distillation takes place rather slowly. When no more distillate comes over when the flask is heated by boiling water the product is shaken with an equal volume of weak sodium carbonate solution in a separating funnel. The carbon dioxide generated must be allowed to escape as described on p. 161, since the pressure generated may otherwise burst the funnel. Next the iodide is shaken with water and then left to stand over fused calcium chloride. The dry liquid is then redistilled from a clean dry distilling flask fitted with a condenser and thermometer. The fraction which comes over between 68° and 73° is retained. Yield about 25 gm. The pure liquid boils at 72°. It darkens in light owing to the liberation of iodine. A dark specimen may be purified by shaking with a little sodium thiosulphate solution to remove iodine, then with water, and then dried over calcium chloride.

Notes. 1. The alkyl iodides are among the most reactive of the alkyl halides, the iodine atom being particularly readily replaced. They are used especially in the preparation of Grignard reagents, which are of great importance in more advanced work.

2. The phosphorus halides are much used to replace hydroxyl groups by halogen (cf. p. 176). In the preparation of chlorides, thionyl chloride SOCl_2 is frequently preferred to phosphorus trichloride (or phosphorus pentachloride) since the by-products are gaseous:



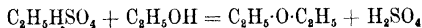
The product is therefore very easily purified (cf. p. 189).

Tests.

The three tests described under Ethyl Bromide can be performed in the same way, using ethyl iodide. The reactions are exactly similar.

Ether (Diethyl ether). $\text{C}_2\text{H}_5\text{O}\cdot\text{C}_2\text{H}_5$.

This particular ether is very readily made by heating a mixture of concentrated sulphuric acid with excess of alcohol. The net result is the removal of H_2O from two molecules of alcohol, a process which can be represented by supposing that ethyl hydrogen sulphate is intermediate:



This, however, may be a simplification of the facts. In any case the method is not a general one since ethers of higher molecular weight have boiling points which are too high for them to be distilled out of the reaction mixture. At high temperatures the reaction of the alcohol with concentrated sulphuric acid produces an olefine, in this case ethylene. A second method (Williamson's method) is therefore afterwards described.

Required:

98 gm. (110 c.c.) absolute alcohol.

75 gm. (40 c.c.) concentrated sulphuric acid.

Method I.

As shown in Fig. 38, a distilling flask of about 500 c.c. capacity is fitted with a double-bored stopper through which pass a thermometer and a tap funnel. The condenser should preferably be of the double surface pattern, but a long Liebig condenser can be used. The receiver is a filter flask to which is attached a length of rubber tubing to convey away the ether vapour from the neighbourhood of all flames. The receiver must make an airtight joint with the condenser, and is cooled in water and, preferably, ice.

In the flask 48 gm. (60 c.c.) of alcohol are mixed with 40 c.c. of concentrated sulphuric acid, the remaining 40 gm. (50 c.c.) of alcohol being placed in the tap funnel. It should be noted that the thermometer bulb

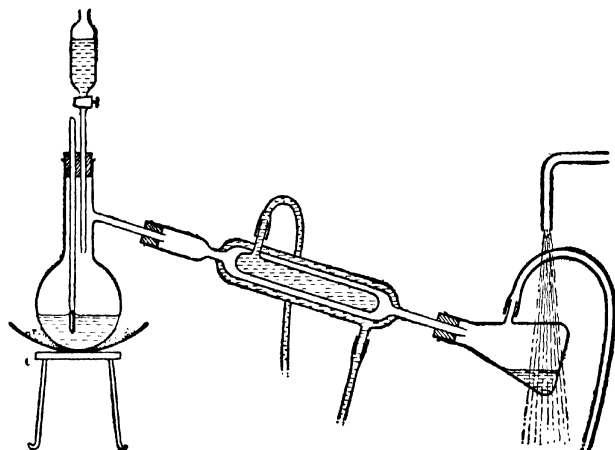


FIG. 38.

is in the liquid. The mixture is heated on the sand bath until the temperature shown by the thermometer reaches 140°C . Alcohol is then run in drop by drop from the funnel at the same speed as the distillate comes over. The temperature should be kept between 140° and 145°C . When all the alcohol has been added this temperature is maintained until no more distillate comes over.

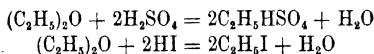
Considerable charring of the alcohol occurs in the course of the experiment. The distillate consists of ether, alcohol and some sulphurous acid—the reduction product of the sulphuric acid by the carbon. It is shaken in a separating funnel with an equal volume of bench caustic soda, separated and then shaken again with the same reagent. The impure ether is left to stand over anhydrous calcium chloride for about an hour. It is then distilled on the water bath, with a filter flask as receiver fitted up as described previously. The distilling flask is best placed in contact

with the water in the water bath after the water has been heated to about 60° to 70°. The Bunsen flame can then be turned out, since no further heating will be necessary. The distillate which comes over between 34° and 39° C. contains a trace of alcohol. This can be removed only by treatment with sodium, followed by redistillation, and for many purposes this is unnecessary. Yield about 30 c.c.

Notes. Ether vapour is extremely inflammable and forms an explosive mixture with air. Great care must always be taken with this substance.

It is used mainly as a solvent in extractions of organic compounds from aqueous solution—not for crystallisation. It is also used in making Grignard compounds.

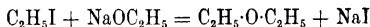
Ether is appreciably soluble in water, and still more so in dilute acids. It is decomposed by concentrated sulphuric acid and by hydriodic acid :



Atmospheric oxidation slowly produces certain explosive peroxides so that the distillation of the ether becomes dangerous.* Shaking with ferrous sulphate solution is a satisfactory method of removing these peroxides.

Method II.

Ethers can be made by the interaction of an alkyl halide with the sodium derivative of an alcohol :



This is a general method, and it can be applied in the preparation of mixed ethers, e.g. $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_7$.

Required :

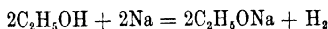
50 c.c. absolute alcohol.

10 c.c. ethyl iodide.

4 gm. sodium.

Ice.

A 150 c.c. round-bottomed flask, fitted with an efficient reflux condenser, is set up for heating on a water bath which at first contains cold water. The alcohol is placed in the flask with some pieces of porous pot and the sodium is added in thin slices, the condenser being momentarily disconnected for each addition. Sodium ethoxide is formed and hydrogen is given off :



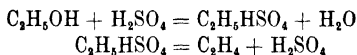
When all the sodium has been added the ethyl iodide is added and the mixture is caused to boil under reflux for about quarter of an hour. The two compounds interact as shown above. Sodium iodide separates.

*The presence of peroxide may be detected by shaking 1 c.c. of ether with a little fresh ferrous ammonium sulphate solution and then adding a few drops of potassium thiocyanate : a blood-red colour shows the presence of peroxide. A blank test should be done on the ferrous salt solution.

The flask is now connected with the condenser by a piece of bent tubing, so that the contents can be distilled on the water bath. A receiver cooled in ice and water must be connected with the condenser as shown in the figure for Method I. The distillate contains some alcohol. This is largely removed by shaking the distillate with an equal volume of strong salt solution in which ether is only slightly soluble. The upper layer of ether is separated and dried by standing over anhydrous calcium chloride in a corked flask. It is then redistilled, following the directions given for Method I. Yield about 20 c.c.

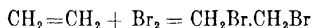
Ethylene and Ethylene Dibromide. C_2H_4 and $C_2H_4Br_2$.

The method by which ethylene is most readily prepared in the laboratory is the dehydration of ethyl alcohol by excess concentrated sulphuric acid:



Ethyl hydrogen sulphate is formed as an intermediate and decomposes at a sufficiently high temperature. The method is not of general application and much alcohol is lost by charring.

Ethylene dibromide is readily formed by addition of bromine across the double bond:



In this experiment the two preparations are carried out simultaneously. If, however, it is desired, gas jars of ethylene may be collected over warm water. The bulb U-tube and conical flask in the figure are then not required.

Required:

- 25 c.c. industrial ethyl alcohol.
- 50 c.c. concentrated sulphuric acid.
- 5 c.c. bromine.
- Ice.

The apparatus is shown in Fig. 39. The wash bottle A contains bench caustic soda. This is to remove sulphur dioxide and carbon dioxide, which are present in the gas given off from the reaction mixture. About 5 c.c. of bromine are placed in the bulb U-tube, and this is cooled by ice and water. The flask B contains a little dilute caustic soda.

The alcohol is placed in the round flask ($\frac{1}{2}$ litre capacity) and the sulphuric acid is added in small portions. The mixture is shaken and cooled under the tap after each addition. Pieces of porous pot are added and the mixture is heated on the sand bath. The thermometer bulb should be in the liquid mixture and a temperature of about 165° or 170° should be maintained. During the evolution of gas the mixture froths and darkens considerably. If ethylene is collected in gas jars it must be remembered that when mixed with air the gas is very explosive.

The preparation of ethylene dibromide proceeds smoothly. Ethylene

is passed through the bromine until bromine vapour is no longer visible over the reddish-brown reaction product. The crude ethylene dibromide is then transferred to a small separating funnel and shaken with water mixed with its own volume of dilute caustic soda. One or two treatments should decolorise the product. The oil is then washed twice with

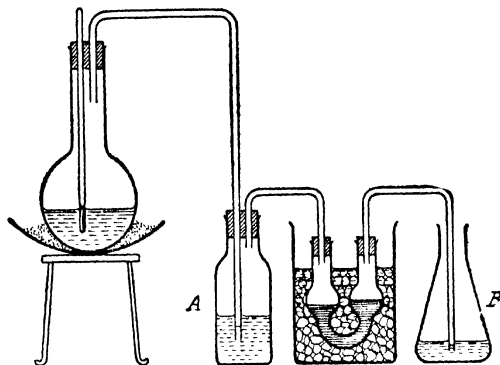
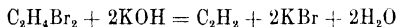


FIG. 39.

a little water and then dried over a few pieces of anhydrous calcium chloride. It is finally distilled, using a small distilling flask attached to a small Liebig condenser. The fraction distilling between 130° and 132° is retained. Yield: nearly equal to the bromine used.

Tests.

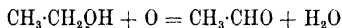
1. A gas jar of ethylene decolorises weak potassium permanganate solution containing a little sodium carbonate (Baeyer's reagent). It is oxidised to ethylene glycol $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}$.
2. A gas jar of the gas decolorises bromine water on shaking. The solution formed does not turn litmus paper red, i.e. no HBr is eliminated.
3. Ethylene dibromide reacts readily with alcoholic potash:



A few pellets of caustic potash are dissolved in a little alcohol by heating. 1 or 2 c.c. of ethylene dibromide are added to the hot solution and acetylene mixed with vinyl bromide $\text{CH}_2 = \text{CHBr}$ is immediately evolved. The gas burns with a smoky, luminous flame.

(Aqueous) Acetaldehyde. $\text{CH}_3\cdot\text{CHO}$.

Moderate oxidation of alcohol by acid dichromate yields acetaldehyde:



Acetaldehyde is itself readily oxidised further to acetic acid, but it may be distilled out of the reaction mixture as it is formed, and in this way

only a little of the aldehyde is lost by oxidation. Aldehydes have lower boiling points than the alcohols from which they are formed.

Required :

17 c.c. concentrated sulphuric acid.

50 gm. sodium dichromate.

40 c.c. alcohol.

The apparatus is the same as that illustrated for the preparation of ether (Method I, p. 164), but in this case the thermometer may be omitted and an adaptor leading into an ordinary conical flask replaces the filter flask. The receiver should be cooled in ice and water. The distilling flask should be of 500 c.c. capacity.

50 c.c. of water and 17 c.c. of concentrated sulphuric acid are mixed in the flask, and some pieces of porous earthenware are added. 50 gm. of sodium dichromate are then dissolved by warming in 100 c.c. of water and, when cool, the solution is mixed with 40 c.c. of alcohol. This mixture is placed in the large tap funnel.

The dilute acid in the flask is first heated to boiling point and then, without further heating, the alcohol-dichromate mixture in the tap funnel is run in little by little. Sufficient heat is evolved for the distillation of acetaldehyde and water to take place. A little acetic acid is always present also in the distillate. The whole of the alcohol-dichromate solution should be added in about 20 minutes, and heat may become necessary to maintain the distillation. The aqueous distillate smells strongly of aldehyde and should be corked up.

The pure aldehyde (b.p. 21°C .) can be obtained from this distillate only by the formation and subsequent decomposition of aldehyde ammonia. This is a tedious process, and the preparation of some aldehyde ammonia from some pure acetaldehyde (which may be purchased) is described instead. The yield of acetaldehyde in the above preparation is poor.

Some acetal, $\text{CH}_3\cdot\text{CH}\begin{matrix} \nearrow \text{OC}_2\text{H}_5 \\ \searrow \text{OC}_2\text{H}_5 \end{matrix}$ is formed by interaction of the aldehyde with excess alcohol, and is present in the distillate.

Tests with aqueous acetaldehyde solution.

1. Aldehydes reduce ammoniacal silver nitrate (Tollen's reagent), giving a silver mirror. Ammonia solution is added drop by drop to some silver nitrate solution in a test tube until the precipitate just redissolves. Equal volumes of this solution and aqueous acetaldehydes are mixed and the test tube containing the mixture is placed in a beaker of hot water. On standing, a mirror of silver is deposited :



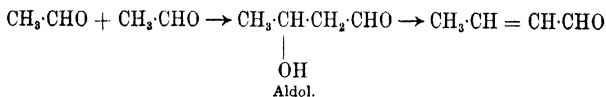
2. Aldehydes also reduce Fehling's solution. Fehling's solution B (Rochelle salt) is added to 5 c.c. of Fehling's solution A (copper sulphate) until the blue precipitate just redissolves. To this solution a few c.c.

of aqueous acetaldehyde are added. On boiling, a red precipitate of cuprous oxide is formed.

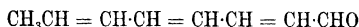
3. Potassium permanganate solution, acidified with sulphuric acid, is decolorised by aqueous acetaldehyde solution. Acetic acid is formed. This is stable to the oxidising agent.

4. A crystal of magenta dissolved in water in a test tube gives a coloured solution which may be decolorised by sulphur dioxide. This solution is called Schiff's reagent. On adding a few drops of the aldehyde solution the colour is restored. (The aldehyde is reduced to alcohol.)

5. To half a test tube of the aqueous solution a small piece of solid caustic soda is added. On warming and then boiling the solution there is a deepening of colour and a brown resinous substance may separate. The aldehyde undergoes self-condensation :

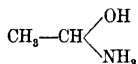


and a repetition of the process leads to the formation of high molecular weight compounds of the form :

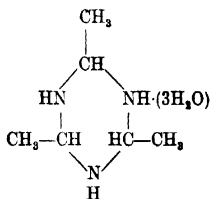


Tests with pure acetaldehyde.

1. Acetaldehyde ammonia. This compound is often written



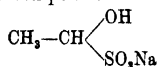
but it is really a trimeric form with the formula



The old formula remains preferable for most purposes. 20 c.c. of 0.88 ammonia solution are placed in a large test tube standing in a large beaker of crushed ice. 10 c.c. of pure acetaldehyde are then added drop by drop. The reaction is vigorous and the mixture must be stirred with a glass rod. On standing in ice for about an hour white crystals of the acetaldehyde ammonia separate. These are filtered at the pump, washed with a little alcohol and then with a little ether, and dried between pieces of filter paper.

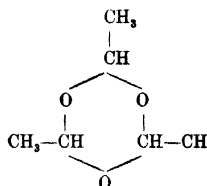
2. Acetaldehyde bisulphite. A solution of sodium bisulphite is made by bubbling sulphur dioxide through some water in a boiling tube, at the

bottom of which is an *excess* of sodium carbonate crystals. The cold saturated solution is apple green in colour and smells strongly of sulphur dioxide. This is shaken with one-third of its volume of pure acetaldehyde. On standing the bisulphite compound

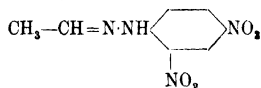


crystallises out.

3. Polymerisation to paraldehyde. A drop or two of concentrated sulphuric acid is added to 1 or 2 c.c. of acetaldehyde in a test tube. Paraldehyde is formed with the production of heat. On adding water it separates as an oil. It has the formula



4. Preparation of a phenylhydrazone. The condensation product of acetaldehyde with phenylhydrazine is an oil, but the product obtained from 2-4-dinitrophenylhydrazine is easily obtained as a yellow crystalline solid, m.p. 146°. 2 to 3 gm. of the dinitro-phenylhydrazine are dissolved in a little warm glacial acetic acid and the solution is added to about 2 c.c. of acetaldehyde in a test tube. The mixture is warmed by placing the test tube in a beaker of warm water for two minutes. On cooling under the tap and on adding a few drops of water while scratching the side of the test tube with a glass rod an orange-red crystalline solid soon separates. This is filtered off and recrystallised from 50 per cent. acetic acid. As obtained in this way the substance has a m.p. of about 146° to 148°. Two isomeric forms appear to exist, one of which has the structure :



(2-4-dinitrophenylhydrazine has many points of superiority over ordinary phenylhydrazine. Its hydrazones are much more readily crystallised, and the reagent does not undergo oxidation on keeping.)

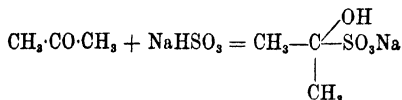
Acetone. $\text{CH}_3-\text{C}-\text{CH}_3$.



Ketones may be made by careful oxidation of secondary alcohols, just as aldehydes are made by oxidation of primary alcohols. Acetone is, however, most readily made by heating calcium acetate :



The decomposition may be carried out by heating the dry salt in a retort. Since acetone is an important industrial solvent its preparation is not described here. It is, however, a useful exercise to prepare pure acetone from the commercial product. A convenient method is to prepare the acetone bisulphite compound and then decompose this with mild alkali.



Some saturated sodium bisulphite solution is made by bubbling sulphur dioxide through 150 c.c. of water in a flask which contains an excess of solid sodium carbonate. The solution should be kept cold by placing the flask in a vessel of cold water. The apple-green solution is decanted into a 500 c.c. flask and shaken with 100 c.c. of acetone, the mixture being kept cool under the tap. The crystalline solid which separates is filtered at the pump and then placed in a half-litre distilling flask. 150 gm. of washing soda and 100 c.c. of water are added and the mixture distilled on the water bath. Acetone (b.p. 56° C.) comes over and is collected and dried over fused calcium chloride or anhydrous sodium sulphate. It is then redistilled.

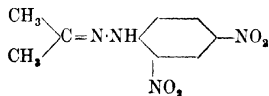
Tests.

1. Acetone does not reduce ammoniacal silver nitrate or Fehling's solution; the coloration of Schiff's reagent takes place only after a time (see tests on acetaldehyde above).

2. A crystalline bisulphite compound is formed. Its preparation has been described above.

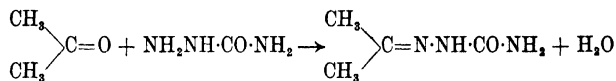
3. Iodoform test. To about 10 c.c. of iodine solution (in potassium iodide) 1 c.c. of acetone is added, and then caustic soda solution is added until the colour of the iodine just disappears. A pale yellow precipitate of iodoform CHI_3 forms on standing. The substance has a characteristic smell. (For alternative method of preparation see p. 173.)

4. Preparation of a phenylhydrazone. The condensation product of acetone with phenylhydrazine melts at 16° and is very difficult to crystallise. The product from 2-4-dinitrophenylhydrazine is easily obtained as a yellow crystalline solid m.p. 126° C. The method of preparation is the same as that described in the case of the acetaldehyde compound, p. 170. The phenylhydrazone should be recrystallised from 50 per cent. acetic acid. It has the structure:



5. Preparation of acetone semicarbazone. Place 2 gm. of semi-carbamide hydrochloride in about 10 c.c. of water and add 2.5 gm. of

crystalline sodium acetate. A clear solution is obtained on warming. 2 or 3 c.c. of acetone are then added and the mixture is warmed by placing the test tube in a beaker of warm water for 10 minutes. The semicarbazone crystallises out on cooling and scratching with a glass rod.



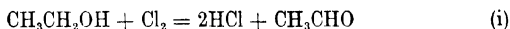
After cooling, the solid is filtered off, washed with water and dried. The pure semicarbazone has a m.p. of 187° C. Alcohol is suitable for recrystallisation.

6. Clemmenson reduction of acetone. Vigorous reduction (by zinc amalgam and strong hydrochloric acid) replaces the carbonyl group of a ketone by the >CH_2 group. Acetone is thus converted into *n*-propane.

To make the zinc amalgam 10 gm. of zinc dust are shaken with about 150 c.c. of mercuric chloride solution for five minutes. The amalgam is washed by decantation and then mixed with 20 c.c. of acetone and 50 c.c. of concentrated hydrochloric acid in a 250 c.c. flask. The flask is heated on the water bath and a delivery tube to a trough of water enables the gas to be collected in gas jars. The smell of the gas, its mode of burning and action on bromine water or Baeyer's reagent should be noted. The last two should, of course, be negative.

Chloroform. CHCl_3 .

By the action of a hypochlorite alcohol is first oxidised to acetaldehyde, and then this compound is immediately chlorinated to give chloral CCl_3CHO . In the presence of alkali this compound is decomposed to give chloroform and a formate:



Reactions similar to (ii) and (iii) take place if acetone is used instead of alcohol.

An aldehyde ($-\text{CH}=\text{O}$) or ketonic ($\text{>C}=\text{O}$) group has a marked "loosening" effect on the hydrogen atoms of the next carbon atom. These are rapidly replaced by chlorine, bromine or iodine.

Required:

100 gm. bleaching powder.

40 c.c. alcohol (or 45 c.c. acetone).

A thin paste of bleaching powder is first made by successive additions of water to the powder, which is placed in a mortar. The mixture is well ground and about 250 c.c. of water is added altogether. This suspension is then decanted into a litre or 1½ litre flask (a bolt-head flask is very convenient). An efficient reflux condenser is then fitted and the apparatus

is set up near a sink or trough full of water, into which the flask may be dipped if the reaction becomes too violent. The alcohol or acetone is then run down the condenser and the contents of the flask are gently shaken. If no reaction commences after five minutes the flask should be warmed *cautiously* on the water bath and immediately removed once signs of effervescence are noticed. The flask may then be clamped in a stand. Alcohol and chloroform condense and run back into the flask while the reaction continues. When the reaction appears to be completed the flask is heated on the water bath for not more than ten minutes.

The reflux condenser is then quickly replaced by a stopper carrying a delivery tube which enables the condenser to be employed for distillation. The chloroform is then distilled off on the water bath. When no more distillate comes over, the product, which usually contains a little acid, is shaken with dilute caustic soda in a separating funnel. The bottom layer is then run out and left to stand over fused calcium chloride. When dry it is transferred to a small distilling flask equipped with a condenser and thermometer. When distilled the fraction coming over between 60° and 63° is retained. Yield about 15 to 20 c.c. The pure liquid boils at 61° C. Its density is 1.50 gm. per c.c.

Iodoform. CHI_3 .

To prepare a specimen of iodoform the best method is to treat acetone with potassium iodide solution in the presence of sodium hypochlorite. Alcohol can be used in place of acetone. The reaction is, in fact, used as a test for the groups $\text{CH}_3\text{C}-$ and $\text{CH}_3\text{CH}_2\text{O}-$ joined to an alkyl or



substituted alkyl group.

Required :

5 c.c. acetone.

15 gm. potassium iodide in 100 c.c. water.

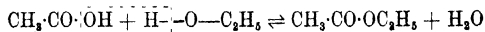
50 c.c. commercial sodium hypochlorite solution.

The acetone and potassium iodide solution are first mixed in a 250 c.c. conical flask. 50 c.c. of bench caustic soda are then added, followed by 50 c.c. sodium hypochlorite, diluted with an equal volume of water. A yellow precipitate of iodoform soon begins to form, and the mixture is left to stand for ten minutes. The solid is then filtered off at the pump and washed with a little water. It is recrystallised from the minimum quantity of hot alcohol. The crystals are dried on a porous plate in a desiccator of calcium chloride. Yield about 5 gm., m.p. 120° C.

Note. The reactions involved are probably similar to those for the formation of chloroform. Although ethyl alcohol gives the iodoform test the aldehyde Cl_3CHO has not been isolated.

Ethyl Acetate. $\text{CH}_3\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$.

The reaction between ethyl alcohol and acetic acid is represented :



The esterification of acetic acid by boiling it with excess alcohol would, however, be an inefficient process. The classic work of Berthelot and de St. Gilles showed that the equilibrium constant for this reaction is

$$\frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = K$$

numerically equal to 4.0. Starting with molar quantities (of either alcohol and acid or ester and water) equilibrium is reached after some days at room temperature, when there is 0.67 mole of ester and 0.67 mole of water present. It follows that if 2 moles of alcohol are added to 1 mole of acid, at equilibrium 0.85 mole of ester and water should theoretically be formed. Since both forward and reverse reactions are catalysed by hydrogen ions, equilibrium may be reached quite quickly if some mineral acid is present. In the Fischer-Speier method of esterification the alcohol is first saturated with hydrogen chloride and then boiled under reflux with the acid. Finally, for practical purposes, it is desirable to make the reaction virtually non-reversible by adding some dehydrating agent to remove the water as it is formed. Anhydrous zinc chloride or concentrated sulphuric acid are commonly used. The latter has the merit that it acts catalytically also.

Required :

50 c.c. absolute alcohol.

50 c.c. concentrated sulphuric acid.

100 c.c. of a mixture of acetic acid and alcohol in equal volumes.

A half-litre distilling flask carrying a tap funnel is fitted to a condenser arranged for distillation (Fig. 40). In the flask is a mixture of 50 c.c. alcohol and 50 c.c. concentrated sulphuric acid. A few pieces of porous earthenware are also added. In the tap funnel is the mixture of alcohol and acetic acid. The flask is heated on an oil bath maintained at 140°. With the flask heated in this way the alcohol-acetic acid mixture is run in at a rate of about three drops a second. As soon as the ester begins to distil over the mixture is run in at the rate at which the ester comes over.

When all the mixture has been added the distillation is continued for a few more minutes, after which nothing more will come over. The distillate contains, in addition to the ester, some unchanged alcohol and acid and some ether and sulphurous acid. Its treatment consists of first shaking it with an equal volume of strong sodium carbonate solution until the upper layer ceases to reddens litmus paper. Much carbon dioxide is evolved, and the pressure in the tap funnel must be released frequently. When all the acid has been neutralised the bottom layer is rejected and a solution of about 40 gm. anhydrous calcium chloride in 40 c.c. water is run in. The ester is shaken vigorously with this solution to remove unchanged alcohol. The lower layer is then run out and rejected, and the ester left to stand over some anhydrous calcium chloride for at least an hour or, preferably, overnight. It is then distilled in a small distilling flask heated on the water bath. If the water bath is heated up from cold

a little ether comes over first (35° – 40°) as a separate fraction. The ester distils between 74° and 79° C. The pure ester boils at 77° C. Yield about 45 gm.

Notes. Ethyl acetate is not a reactive compound but it finds use in synthetic work :

(a) In the preparation of acetoacetic ester, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$.

(b) In reaction with Grignard compounds, e.g. in making certain ketones and tertiary alcohols.

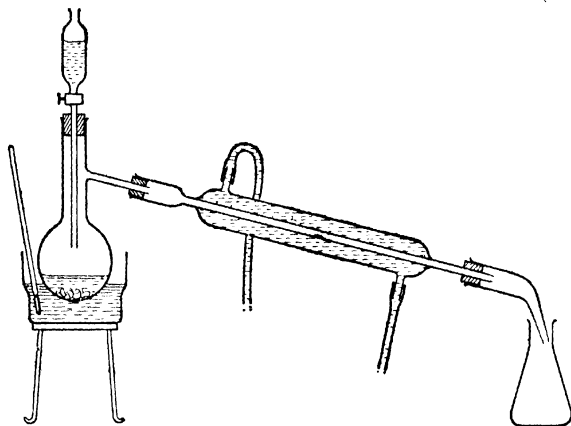


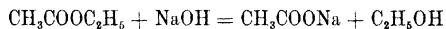
FIG. 40.

Hydrolysis of Ethyl Acetate.

This experiment may be regarded as indicating the method of hydrolysis of esters in general. See, in addition, p. 189.

5 or 10 c.c. of the ester are boiled under reflux with about 50 c.c. of bench caustic soda. Pieces of porous earthenware are essential to avoid bumping. After quarter of an hour there should be no longer two distinct layers. On replacing the condenser in the position for distillation and distilling the mixture, aqueous alcohol comes over first. After 5 or 10 c.c. of distillate have been collected it may be subjected to the iodoform test.

If some bench sulphuric acid is added to the residual liquid in the flask acetic acid is liberated and may be recognised by its smell.

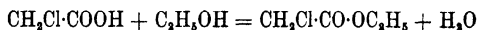


When the acid liberated is a solid it is filtered off and recrystallised.

Ethyl Chloroacetate. $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$.

This ester, which is important in synthetic work, may be made as an alternative to the preceding compound. Monochloroacetic acid is

a somewhat tedious preparation and it is, in any case, an inexpensive chemical. It is a much stronger acid than acetic acid.



Required :

30 gm. monochloroacetic acid.

45 c.c. absolute alcohol.

6 c.c. concentrated sulphuric acid.

The alcohol is placed in a small round flask and the sulphuric acid added, taking the usual precautions. The chloroacetic acid is then added. The mixture is heated on the water bath, using a reflux condenser for about six hours. Owing to the high boiling point of the ester it is not practicable to remove it by distillation as in the previous preparation. Instead, the mixture is poured into a beaker containing about 100 c.c. of cold water and preferably a little ice.

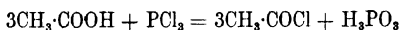
The mixture of ester and water is then transferred to a separating funnel and shaken with about 100 c.c. of ether. The lower layer is run out into a beaker and the top layer retained. The lower layer is then extracted once more with a further 50 c.c. of ether and the two upper layers are united. The lower layer, after the second extraction, is rejected.

The combined ether extracts are then left in a stoppered flask containing fused calcium chloride. When dried the ether solution is placed in a distilling flask fitted with a thermometer and an efficient condenser and heated on the water bath. The usual precautions for distilling ether (p. 164) must be observed. When all the ether has been distilled off the temperature of the water bath is raised to boiling point. To distil the ester the flask must be fitted with an air condenser and heated with a naked flame. Ethyl chloroacetate distils between 144° and 146° . A yield of about 25 gm. is obtained.

Notes. Ethyl chloroacetate (chloroacetic ester) is used in the preparation of malonic and cyanoacetic esters. These, like acetoacetic ester, are of importance in more advanced synthetic work.

Acetyl Chloride. $\text{CH}_3\cdot\text{COCl}$.

Compounds containing hydroxyl groups react with phosphorus trichloride or with thionyl chloride, with the result that the hydroxyl group is replaced by a chlorine atom. Carboxylic acids are by this means converted into their acid chlorides :



Acetyl chloride is volatile and is easily distilled from the non-volatile phosphorus acid. Thionyl chloride, because of its volatility, would not be a convenient reagent in this particular case.

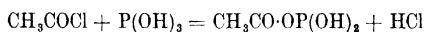
Required :

50 c.c. glacial acetic acid.

40 gm. (25 c.c.) phosphorus trichloride.

The apparatus consists of a 250 c.c. distilling flask fitted with a tap funnel and a condenser which leads through a rubber stopper into a small filter flask which acts as a receiver. The latter is fitted with a calcium chloride exit tube. The apparatus should be quite airtight and perfectly clean and dry. The acetic acid is placed in the distilling flask, which is kept cold by being placed in cold water in a water bath standing on a tripod. The phosphorus trichloride is then run in slowly from the tap funnel.

When the phosphorus trichloride has all been added, the water in the water bath is heated to about 40° or 50° C. and kept at this temperature until the evolution of hydrogen chloride begins to slacken. This is due, probably, to a reaction:



The originally homogeneous liquid forms two separate layers. At this stage the temperature of the water bath is raised to boiling point to distil off the acetyl chloride which forms the top layer. (It is *dangerous* to effect this distillation with a flame instead of using a water bath.) When nothing further comes over, the distillate is redistilled and the fraction boiling between 53° and 56° is retained. Yield about 40 gm. The liquid fumes strongly in air, and must be kept in a sealed tube. Boiling point of the pure liquid, 55° C.

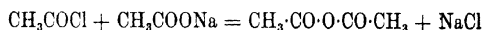
Note. With the removal of the hydroxyl group and its replacement by chlorine the hydrogen atoms in the molecule become much more reactive. The acid chloride is readily chlorinated or brominated, a fact which is utilised in the method of making α -brom acids due to Hell, Volhard and Zelinsky. In this method the acid is treated with red phosphorus and excess bromine. The acid bromide is formed first, and this is then immediately brominated. The α -substituted acid bromide may then be hydrolysed to the acid.

Tests.

See p. 178 for tests which may be carried out on acetyl chloride and acetic anhydride.

Acetic Anhydride. $\text{CH}_3\text{CO-O-CO-CH}_3$.

The chlorine atom of acetyl chloride is only loosely held and is readily replaced, e.g. in hydrolysis and in the acetylation of amines (tests below). When heated with sodium acetate there is an elimination of sodium chloride and acetic anhydride is formed:



This compound is distilled off.

Required:

25 gm. anhydrous (fused) sodium acetate.

20 c.c. acetyl chloride.

If fused sodium acetate is not available 50 gm. of the crystalline salt, M.P.C.

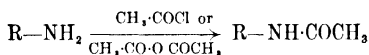
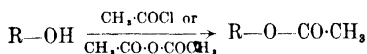
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$; are melted in a clean iron sand tray. When heated the salt first melts and then, losing water, solidifies. On stronger heating the solid again melts. The solid is finely powdered when cold.

The experiment should be carried out in a fume chamber. The sodium acetate is placed in a 250 c.c. retort which is attached to a condenser and receiver, fitted with a calcium chloride exit tube as in the previous experiment. All joints must be airtight, and the apparatus must be clean and dry. A dropping funnel containing the acetyl chloride is inserted through a cork in the tubulure of the retort.

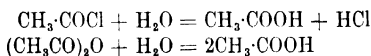
When the acetyl chloride is slowly run into the retort heat is produced, but nothing should distil over. If necessary the retort may be cooled in water. After the addition of the acetyl chloride a glass rod is inserted through the tubulure and the contents of the retort are well mixed. The retort is then closed with an ordinary cork or glass stopper, and the mixture is heated evenly with a small flame. The distillate obtained contains a good deal of unchanged acetyl chloride, and it is essential to pour it back into the retort and repeat the distillation. The product is then redistilled, using a clean dry distilling flask of 100 c.c. capacity. Acetic anhydride comes over between 130° and 140° . Yield about 20 gm. The pure liquid boils at 140°C .

Tests with acetyl chloride and acetic anhydride.

These compounds have similar uses in synthetic work. They are especially used to replace the hydrogen atom of either an hydroxyl group or one of the hydrogen atoms of an amino group by the acetyl group :

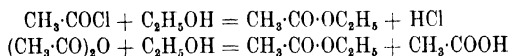


1. Warm a few drops of either compound with some water in a test tube. Acetic anhydride is hydrolysed more slowly.



Solution reacts acid to litmus and, in the case of acetyl chloride, the presence of chloride ion can be demonstrated.

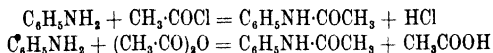
2. Repeat the experiment with a little alcohol :



The smell of ethyl acetate may be recognised.

3. If a little aniline is dissolved in some glacial acetic acid and boiled with a little of either acetyl chloride or acetic anhydride, acetanilide is formed. On pouring the mixture into water the acetanilide separates as a white solid. To prepare the substance in any quantity it is neces-

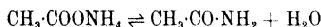
sary to boil the mixture in a flask fitted with a reflux condenser for about half an hour.



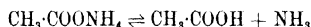
The solid may be recrystallised from hot water, m.p. 112°C .

Acetamide. $\text{CH}_3\text{CO}\cdot\text{NH}_2$.

Amides are, in general, most often made by the action of ammonia on either the acid chloride or an ester of the acid in question. These methods are illustrated in the preparation of oxamide and benzamide given below. In the case of acetamide the dehydration of ammonium acetate is in practice a very satisfactory method and it is the one most often used for this compound.



The reaction is reversible, so the water is removed as it is formed. A good yield is obtained only if the dissociation of the salt :



can be prevented. Addition of excess of acetic acid has the effect of reducing this change to small proportions.

Required :

50 gm. ammonium acetate.

60 gm. (58 c.c.) glacial acetic acid.

A 250 c.c. round-bottomed flask is fitted with an air condenser (Fig. 41). In the upper end of the condenser is a thermometer reading to not less than 150°C . and a bent delivery tube for conducting away steam and acetic acid vapour. By boiling the mixture of ammonium acetate and acetic acid so that the temperature at the top of the condenser is between 103° and 105° , a proportion of the water formed in the change is removed from the reaction mixture.

After two hours' heating the reflux condenser is removed and replaced in the position for distillation. If a short fractionating column is available it should be used in conjunction with the air condenser. The distillate, which comes over up to a temperature of 170° to 180° , is then collected. This consists mainly of acetic acid and water.

At this point the residue is poured while hot into a 100 c.c. distilling flask fitted with an air condenser. On continuing the distillation acetamide is collected in the fraction which distils between 210° and 225° .

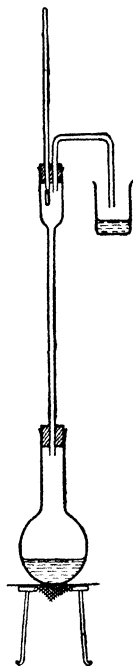


FIG. 41.

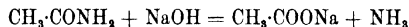
The distillate should be collected in a small clean flask or a large test tube. On cooling the substance solidifies. There may be some solidification in the air condenser, but this is easily removed by warming with the flame.

The substance obtained in this way smells of mice. A pure specimen, lacking this quality, can be prepared by recrystallisation from benzene or acetone. It has then a m.p. of 82° and a b.p. of 223° .

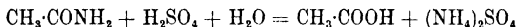
Tests.

Amides are sometimes used as derivatives in the identification of acids, since they are well crystallised solids and readily hydrolysed back to the acid.

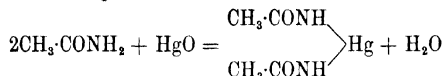
1. A little acetamide is warmed with some bench caustic soda. Ammonia is evolved:



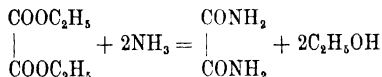
If the amide is boiled with bench sulphuric acid the smell of acetic acid may be detected:



2. The acidic character of acetamide is weak. The solution in water will, however, dissolve precipitated mercuric oxide. If a little sodium carbonate solution is added to some mercuric chloride, mercuric oxide is precipitated. On adding a strong solution of acetamide in water the precipitate dissolves up.

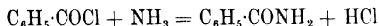


Oxamide may be made on a small scale by adding a few drops of strong (0.88) ammonia solution to about 1 c.c. of ethyl oxalate in a test tube.



The mixture requires stirring with a glass rod. The amide separates and is stirred with a few c.c. of water before filtering on a small Buchner filter at the pump. After washing with a little water the solid is dried on a porous plate or with filter paper before being placed in the steam oven. Oxamide has not a sharp melting point; on heating it decomposes with some sublimation at a high temperature.

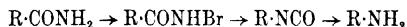
Benzamide may be made by grinding 10 gm. of ammonium carbonate with 5 c.c. of benzoyl chloride in a mortar (fume chamber).



After ten minutes a few drops of 0.88 ammonia solution are added if the smell of benzoyl chloride still remains. The mixture is then stirred into 100 c.c. of cold water and then filtered. The solid is crystallised from hot water, m.p. 128°C .

Methylamine Hydrochloride. $\text{CH}_3\text{NH}_2\cdot\text{HCl}$.

Alkyl (and aryl) amines may be obtained from amides by Hofmann's reaction, which consists of treatment of the amide with bromine and caustic potash. The intermediate bromamide appears to lose HBr and to undergo rearrangement to the isocyanate. This is hydrolysed to the amine which has one fewer carbon atoms than the original amide.

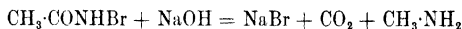


There is some loss of amide through hydrolysis by the caustic alkali, and the preparation is a little difficult.

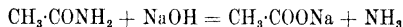
Required :

- 20 gm. dry acetamide.
- 54 gm. (18 c.c.) bromine.
- 80 gm. caustic potash.
- Absolute alcohol.

The acetamide and bromine are placed in a 500 c.c. flask. The flask is cooled under the tap while a solution of 20 gm. caustic potash in 200 c.c. of water is added slowly. The solution is finally yellow and contains the bromamide. This is then run slowly from a tap funnel into a concentrated solution of 60 gm. caustic potash in 100 c.c. water in a large distilling flask. During this operation care must be taken to see that the temperature does not rise above 75°C . The solution is then kept for about half an hour at between 60° and 70°C . After this time the yellow colour will have disappeared, and the mixture can be distilled on a wire gauze to drive off the amine.



Some ammonia is also generated by decomposition of some unchanged amide :



The mixed gases, methylamine and ammonia, are absorbed in 100 c.c. of dilute hydrochloric acid. For this purpose a bent adaptor dipping into the acid is connected to the end of the condenser.

When no more alkaline distillate comes over, the solution in hydrochloric acid is evaporated to dryness in an evaporating dish. The residue consists of methylamine hydrochloride and ammonium chloride. Extraction with absolute alcohol separates the methylamine hydrochloride, and this crystallises out from the alcohol solution on cooling. A further quantity may be obtained by evaporation. The crystals are dried in a desiccator. Yield about 5 gm., m.p. 226°C .

Tests.

1. The free amine is liberated by warming the hydrochloride with a little caustic soda. Its smell resembles that of ammonia, but is slightly fish-like. The vapour is inflammable.

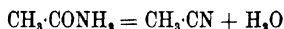
2. If a strong solution of picric acid in alcohol is added to an aqueous

solution of methylamine the mixture turns red. After warming for two minutes the solution is cooled at the tap and then the tube is scratched with a glass rod. A yellow picrate of the base crystallises out and may be filtered off; m.p. 210°C . It may be recrystallised from alcohol.

Note. Methods of identifying primary, secondary and tertiary amines are described in connection with aniline, methylaniline and dimethylaniline, p. 197.

Acetonitrile. $\text{CH}_3\cdot\text{CN}$.

The dehydration of an amide to give the corresponding nitrile is readily brought about by phosphorus pentoxide.



Required :

20 gm. dry acetamide.

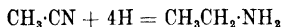
30 gm. phosphorus pentoxide.

A clean dry distilling flask of 200 c.c. capacity is first fitted with a 100° thermometer and a condenser. 20 gm. of *dry* acetamide are then weighed out on a piece of paper. The flask is then roughly weighed and approximately 30 gm. of phosphorus pentoxide are transferred direct from the bottle, so that there is an appropriate gain in weight. The 20 gm. of acetamide are then quickly added and the flask is well shaken. The condenser and thermometer are fitted without delay and, with a small luminous flame, the mixture is carefully heated as evenly as possible. Frothing accompanies the reaction, and for five or ten minutes stronger heating should not be attempted. The acetonitrile is then driven over with the help of a hotter flame.

The crude distillate obtained is mixed with half its volume of cold water, and then solid potassium carbonate is added until no more will dissolve in the lower (aqueous) layer. The liquid is then decanted into a separating funnel and the lower layer is run off and discarded. The nitrile is redistilled from a small distilling flask, in which is placed a little phosphorus pentoxide. The acetonitrile, which has a peculiar smell, comes over at 82° . Yield about 5 gm.

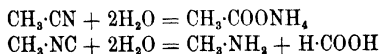
Test.

If a little acetonitrile, dissolved in absolute alcohol, is treated with sodium in small pieces it is reduced to ethylamine :



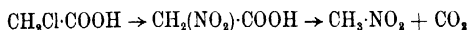
The presence of the primary amine may be shown by the carbylamine reaction (cf. p. 192).

Note. Nitriles may be hydrolysed by either aqueous alkali or dilute acid. Isonitriles are stable towards alkalis; dilute acids convert them into primary amines plus formic acid :



Nitromethane. $\text{CH}_3\cdot\text{NO}_2$.

The aliphatic nitro-compounds are not so accessible as the corresponding aromatic compounds. Direct nitration of aliphatic hydrocarbons gives a poor yield, and these compounds are usually obtained through the alkyl halides or, better, from the α -substituted fatty acids:



The nitro-acids readily decompose on heating.

Required :

50 gm. monochloroacetic acid.

30 gm. anhydrous sodium carbonate, or 75 gm. washing soda crystals.

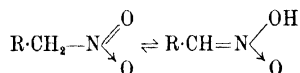
36 gm. sodium nitrite.

The chloroacetic acid is first dissolved in 100 c.c. of water in a litre distilling flask and, by the addition of the sodium carbonate in small quantities, the solution is made slightly alkaline. The apparatus is then set up for distillation and a tap funnel is inserted through a cork in the neck of the distilling flask. A solution of 36 gm. of sodium nitrite in 50 c.c. of water is then run in and the mixture is heated over a wire gauze.

Evolution of carbon dioxide and the appearance of a red colour accompany the distillation of nitromethane and water which come over together. The distillation is continued until no more oily drops sink to the bottom of the receiver. The slightly red-coloured nitromethane is separated by means of a separating funnel and dried over anhydrous calcium chloride or sodium sulphate. It is then distilled in a small distilling flask. The liquid boils at 101° – 102° C. Yield about 15 gm.

Notes.

1. Aliphatic nitro-compounds and some aromatic nitro-compounds behave as tautomeric substances:

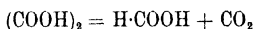


The second is the "nitrolic acid" form.

2. The hydrogen atoms attached to the α -carbon atom of an aliphatic nitro-compound are markedly reactive through being "loosened" by the nitro group. They are readily replaced by chlorine, and also permit of interesting condensations, e.g. with aldehydes (cf. p. 206).

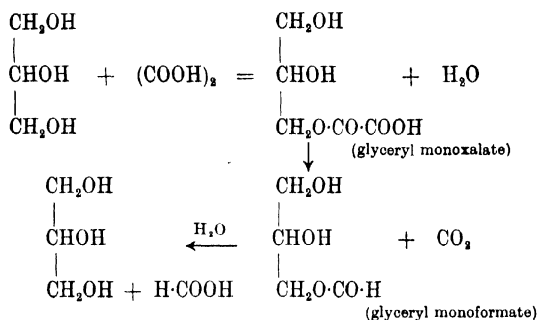
Formic Acid (Aqueous). $\text{H}\cdot\text{COOH}$.

In the laboratory formic acid is derived from oxalic acid. The yield obtained by heating the latter acid alone is poor:



Some of the oxalic acid decomposes into carbon monoxide, carbon dioxide

and water, and some sublimes unchanged. A mixture of glycerol and excess oxalic acid on heating yields formic acid through a series of changes :



The glycerol is, theoretically, not consumed. The water necessary for the hydrolysis of the monoformate comes from the original esterification and from the water of crystallisation of oxalic acid.

Required :

50 c.c. anhydrous glycerol.

30 gm. powdered crystalline oxalic acid.

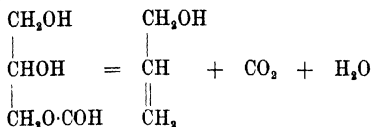
Since glycerol is very hygroscopic the sample used should be dehydrated. 70 c.c. of glycerol are heated in a large evaporating basin on a wire gauze or sand bath and stirred with a thermometer until the temperature reaches 175° or 180° C. This temperature is maintained for about five minutes, after which the water will have been driven off.

While the glycerol is still warm (about 60°), 50 c.c. of it are poured into a retort or a 250 c.c. distilling flask containing 30 gm. of powdered oxalic acid. A thermometer should be inserted through a cork and its bulb should be immersed in the reaction mixture. The retort or flask is fitted with a condenser arranged for distillation, and then the temperature is raised by heating evenly with a small naked flame. The temperature of the mixture must be kept between 100° and 110° during the time that effervescence continues. A small amount of distillate will be obtained. A further quantity of oxalic acid is added when the reaction slackens, and this process is repeated if necessary until sufficient aqueous formic acid has been collected.

The aqueous distillate cannot be concentrated by an ordinary distillation process since formic acid boils at 101° C. The solution is therefore best used for carrying out the tests on formic acid described below. Lead or copper formate may, however, be made by adding the metallic carbonate in excess, filtering and evaporating to the point of crystallisation.

Allyl Alcohol. If the residual reaction mixture is heated more

strongly so that a temperature of 190° to 200° C. is attained, a small amount of allyl alcohol (b.p. 96°–97° C.) is formed :



The liquid has a very irritating smell. It responds to the tests for unsaturation (p. 212).

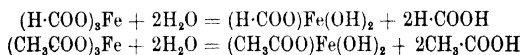
Tests with Acetic and Formic Acids.

Except where stated these tests can be carried out on a moderately strong aqueous solution of the acid.

1. These acids react in the usual manner with either caustic soda or sodium carbonate solution. In the latter case carbon dioxide is evolved.

2. The acids form esters when warmed with a little ethyl alcohol and a few drops of concentrated sulphuric acid. To a little of the acid (glacial acetic acid or 90 per cent. formic acid)—or a little of the solid sodium salt—1 or 2 c.c. of ethyl alcohol are added. A few drops of concentrated sulphuric acid are necessary to hasten the reaction. After warming gently for one minute and then adding an equal volume of water the characteristic smell of the ester will be noticed: ethyl acetate smells of apples, the formate of rum.

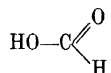
3. A little of the acid is neutralised with bench caustic soda—or more conveniently, the sodium salt is dissolved up—and neutral ferric chloride is added drop by drop. Both formate and acetate solutions give a deep red coloration which changes on boiling when the reddish-brown basic ferric salt is precipitated. The change may be represented :



4. Formic acid possesses certain distinguishing features :

- (a) The 90 per cent. acid, or solid sodium formate, when warmed with a little concentrated sulphuric acid, gives carbon monoxide.
- (b) A solution of formic acid or sodium formate will reduce mercuric chloride solution on warming to mercurous chloride (white ppt.) and a little free mercury (grey ppt.) may be formed.
- (c) If a few drops of potassium permanganate are added to a solution of formic acid containing a little dilute sulphuric acid, the colour of the permanganate is discharged slowly on warming.
- (d) If an alkaline solution of formate is used for the preceding experiment the colour of the permanganate is immediately discharged. A ppt. of manganese dioxide is formed.
- (e) On adding a few drops of neutral sodium formate solution to a little ammoniacal silver nitrate solution, a grey ppt. of silver, or a silver mirror, is produced in the cold.

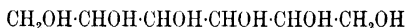
Reactions (b) to (e) probably result from the "aldehydic" structure of formic acid :



The existence of the $-\text{CH}=\text{O}$ group may explain the reducing action of the acid.

Hexacetyl Mannitol.

Mannitol is a hexahydric alcohol with the formula



It forms esters with certain acids, these being made by the action of the acid chloride or the acid anhydride.

Required :

- 5 gm. mannitol
- 20 c.c. acetyl chloride
- 20 c.c. glacial acetic acid.

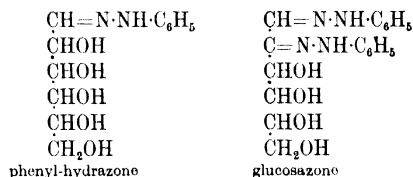
N.B.—Do this experiment in a *fume chamber*.

The mannitol and acetic acid are mixed in a small round flask (250 c.c.) and a reflux condenser is ready to put in position. 20 c.c. acetyl chloride are then added and the condenser placed in position. A reaction quickly begins, with production of heat and evolution of HCl gas. After this has subsided the flask is heated on a wire gauze over a small flame for about ten minutes, the mixture being kept at the boiling point. Quantities of HCl gas are given off.

The mixture is then poured, while hot, into 100 c.c. of cold water in a beaker and left to stand. The ester separates as a white solid after some time. It is filtered at the pump and recrystallised from a little alcohol. M.p. 119°C . Yield about 8 gm.

Glucosazone.

Glucose readily condenses with phenylhydrazine to form the glucosazone (instead of the simpler phenyl-hydrazone) :



Required :

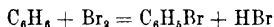
- 2 gm. glucose (or fructose)
- 4 c.c. glacial acetic acid in 10 c.c. water.
- 4 c.c. phenylhydrazine.

2 gm. glucose are dissolved in 10 c.c. water in a boiling tube. In another tube 4 c.c. acetic acid, 10 c.c. water and 4 c.c. phenylhydrazine are shaken to give a clear solution. The two solutions are mixed, stirred, and the mixture heated in a boiling water bath or beaker of water. After about 20 minutes the yellow osazone begins to crystallise out. After 30 minutes the mixture is cooled and filtered on a small Buchner funnel. The solid is washed with a little water, then with a little alcohol, and drained thoroughly.

The osazone can be recrystallised from acetic acid, and the crystals washed with a little cold alcohol. M.p. 210°C . (with decomposition).

Bromobenzene. $\text{C}_6\text{H}_5\text{Br}$.

Bromobenzene and chlorobenzene can be made by direct substitution using a halogen carrier. Iodobenzene can also be made directly, but the reaction is slow and the alternative method, starting with aniline, is described on p. 195.



Required :

22 gm. (25 c.c.) benzene.

54 gm. (18 c.c.) bromine.

0.5 c.c. pyridine.

The three substances are mixed in a 150 c.c. flask fitted with a reflux condenser, and then heated in a water bath kept at 25° to 30° in a fume chamber. Fumes of hydrogen bromide are evolved and these may, if desired, be absorbed in some water, using a delivery tube and an inverted funnel connected to the top of the condenser. After about an hour the temperature of the water bath is gradually raised to 65° or 70°C .

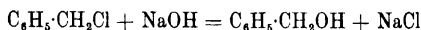
When the evolution of acid fumes slackens and most of the bromine has disappeared, the flask is cooled and the contents are poured into a beaker containing about 100 c.c. of bench caustic soda. The mixture is then transferred to a separating funnel and shaken up. If, after separating the two layers, the upper (aqueous) layer gives an acid reaction to litmus paper, the bromobenzene is again washed with alkali. The bottom layer is then run off and dried over anhydrous calcium chloride or anhydrous sodium sulphate and then distilled, using an air condenser. A little unchanged benzene comes over first (b.p. 80.5°C .) and then the fraction boiling between 150° and 160° is collected separately. Yield about 20 gm. The pure compound has a b.p. of $154^{\circ}-5^{\circ}\text{C}$. and has a pale yellow colour. Its smell somewhat resembles that of benzene.

Note. The halogen atom is not removed by the action of either aqueous or alcoholic caustic potash and the compound is somewhat inert. The presence of an *ortho* or *para* nitro group renders the halogen atom much more reactive.

Benzolc acid by oxidation of Benzyl Chloride. $\text{C}_6\text{H}_5\text{COOH}$.

The benzene nucleus (except when "activated," cf. p. 193) is stable to all but the very strongest oxidising agents. An alkyl group attached

to a benzene nucleus is, however, a readily oxidised "side-chain." Oxidation by alkaline permanganate converts such a side chain into a carboxyl group. Unfortunately toluene, the simplest compound for illustrating this change, is immiscible with aqueous solutions, and the oxidation proceeds very slowly. Benzyl chloride, made by chlorinating toluene in sunlight, is much more readily oxidised, presumably because benzyl alcohol is first formed by hydrolysis:



and this is soluble in water.

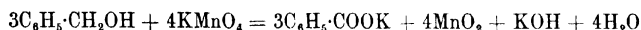
Required :

10 gm. potassium permanganate.

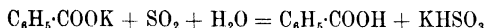
5 gm. anhydrous sodium carbonate.

5.5 gm. (5 c.c.) benzyl chloride.

These substances are placed in a half-litre flask fitted with a reflux condenser and 200 c.c. of water are added. The mixture is then boiled with a few pieces of porous pot on a wire gauze. The oxidation of the compound requires at least an hour, and it may be judged to be complete when no more oily drops of unchanged benzyl chloride can be seen in the condenser. Manganese dioxide is formed as a dark precipitate.



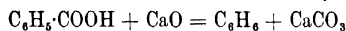
To remove the precipitate (and any excess potassium permanganate) sulphur dioxide from a bottle is bubbled through the solution. The manganese dioxide forms manganese sulphate and benzoic acid separates on cooling.



The acid is filtered off and recrystallised from hot water. Yield about 4 gm., m.p. 121° C.

Test.

If an intimate mixture of benzoic acid and fresh quicklime is heated in a dry test tube benzene is formed. Excess of quicklime should be used and the test tube should be fitted with a right-angle delivery tube connected to a small condenser or dipping into a test tube surrounded with cold water.



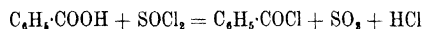
The benzene may be recognised by its smell and by a determination of its boiling point by a semi-micro boiling-point method.

Determination of Boiling Point. A small test tube or ignition tube of about quarter of an inch diameter is attached by a rubber band (near the rim) to a thermometer which is arranged as for the determination of melting points (p. 158). The specimen of benzene is placed in the small test tube and heated by the paraffin of the melting-point bath (Fig. 42). The temperature must be raised *very* slowly and the bath is

kept stirred. An empty melting-point tube is placed in the test tube with its open end at the bottom. At the boiling point of the benzene (80.5° C.) a steady stream of bubbles is produced at the open end of the capillary tube.

This is a "micro" method. If 2 or 3 c.c. of the liquid are available, a much more accurate b.p. can be found by using an ordinary test tube and placing the bulb of the thermometer in the liquid. The test tube should not rest on the bottom of the heating bath. The temperature recorded by the thermometer will not then go above the boiling point.

Conversion of Benzoic Acid to Benzoyl Chloride. On a small scale this may be done by adding enough thionyl chloride to about 0.5 gm. benzoic acid in a test tube to give a thin paste. The test tube is loosely plugged with a cork and heated for about ten minutes in boiling water (fume chamber). Sulphur dioxide and hydrogen chloride are evolved:



Excess thionyl chloride (b.p. 77°) is vaporised. On adding a little water to the residue the oily nature of the product may be seen. It has the characteristic smell of benzoyl chloride.

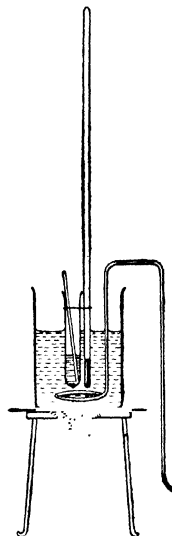


FIG. 42.

Ethyl Benzoate. The preparation of this ester illustrates the important catalytic method of esterification due to Fischer and Speier. 20 gm. of benzoic acid are dissolved in 60 c.c. of absolute alcohol in a round-bottomed flask, and a steady stream of HCl gas is blown through the solution (fume chamber). The HCl gas may be made by dropping concentrated sulphuric acid on salt. After passing the gas for about half an hour the flask is fitted with a reflux condenser and heated gently on a sand bath so that the mixture is kept gently boiling for about 1½ hours. After this time the excess alcohol is removed by distillation (b.p. alcohol 78°, ethyl benzoate 213° C.), but before distilling the benzoate it must be washed with dilute sodium carbonate solution and then with water. The separation of the ester from these aqueous layers is assisted by adding a little chloroform or carbon tetrachloride. The lower layer is then run off and finally dried over calcium chloride and distilled. (Hydrolysis, see below.)

Hydrolysis of an Ester of an Aromatic Acid.

• Required :

12 c.c. methyl salicylate (oil of wintergreen).

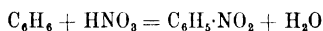
100 c.c. of approx. 2N caustic soda solution.

The two substances are mixed in a round flask of about 300 c.c. capacity fitted with a reflux condenser and heated on a wire gauze. A little porous pot is added and the mixture is kept steadily boiling for about quarter of an hour. At the end of this period there should be no smell of the ester. The solution is cooled and placed in a large beaker. On making the solution acid with bench hydrochloric acid the free salicylic acid separates out. It is filtered at the pump and then recrystallised by boiling with a large quantity of water and leaving to cool. The crystals, when filtered and dried in the oven, have a m.p. of 157°.

Methyl or ethyl benzoate can be used for the experiment, but a longer period of boiling under reflux is required, this being continued until there are no oily drops visible in the condenser. M.p. benzoic acid 121° C.

Nitrobenzene. $C_6H_5 \cdot NO_2$.

In the presence of concentrated sulphuric acid, concentrated nitric acid is a nitrating agent towards aromatic hydrocarbons. The role of the sulphuric acid is (i) to bring the reactants into the same phase, (ii) to provide nitric acid in a more or less anhydrous state and to prevent dilution of this acid as the reaction proceeds.



Although the reaction is not reversible the dilution of the nitric acid is undesirable, since the dilute acid functions mainly as an oxidising agent.

Required :

- 50 gm. (57 c.c.) benzene.
- 60 c.c. concentrated nitric acid.
- 60 c.c. concentrated sulphuric acid.

The sulphuric acid is added to the nitric acid in a 250 c.c. flask, which is gently shaken and cooled under the tap. The cold mixed acid is then added in small portions to the benzene, which is placed in a half-litre round-bottomed flask. The mixture must be well shaken after each addition, and the temperature must not be allowed to go above 50°–60° C. to avoid formation of dinitrobenzene. It is necessary, therefore, to cool the flask under the tap during the nitration, which proceeds with the evolution of brown fumes. About twenty minutes' are needed for the process. The flask is then placed in a water bath at 60° or 70° C. for about half an hour. It requires to be shaken from time to time, since the substances form two layers at this stage.

The flask is then emptied into a beaker containing about 300 c.c. of cold water, and the nitrobenzene separates as a dense oil at the bottom. After pouring off some of the supernatant liquid the remainder is separated, using a separating funnel, the bottom layer being preserved. The nitrobenzene is then shaken in the funnel with water, and then with sodium carbonate solution (about 10 gm. in 100 c.c.). After standing for

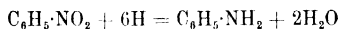
some minutes the two layers are separated as completely as possible, and the nitrobenzene, without washing with water, poured into a small conical flask containing some anhydrous sodium sulphate or calcium chloride. When dry it is decanted into a 100 c.c. distilling flask fitted with an air condenser. It is distilled by heating with a naked flame, and the fraction which comes over between 206° and 210° is collected in a separate receiver. Yield about 50 gm. The b.p. of the pure liquid is 209°–210° C. It smells of almonds.

The dark brown residue in the distilling flask is dinitrobenzene. It should not be heated strongly so as to avoid charring and subsequent difficulty in cleaning.

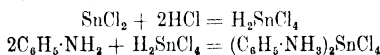
Note. Nitrobenzene is not a reactive substance, and apart from its use in the manufacture of aniline it is mainly of interest as a solvent, e.g. in carrying out the Friedel and Craft's reaction. It has a high dielectric constant and dissolves electrovalent compounds to some extent.

Aniline. $C_6H_5NH_2$.

Aromatic nitro-compounds may be reduced to the corresponding amines by the use of tin and concentrated hydrochloric acid or by iron filings and concentrated hydrochloric acid (Béchamp) and other vigorous reducing agents.



Using tin and hydrochloric acid, aniline forms a salt which must afterwards be decomposed by alkali:



Required:

25 gm. (21 c.c.) nitrobenzene.

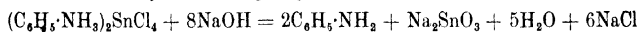
50 gm. granulated tin.

100 c.c. concentrated hydrochloric acid.

75 gm. caustic soda in 100 c.c. water.

The nitrobenzene and tin are placed in a litre round-bottomed flask fitted with a reflux condenser. The concentrated hydrochloric acid is added in small quantities at intervals down the condenser so that a brisk reaction is maintained for some time. The flask should be shaken from time to time. When the reaction between the acid and the tin has subsided the condenser is removed and the flask is heated on the water bath for about twenty minutes. This completes the reduction and vaporises unchanged nitrobenzene in the steam. There should finally be only a faint smell of nitrobenzene.

The aniline is liberated from its salt by adding the caustic soda solution. Stannic hydroxide is precipitated at first but redissolves.



The only satisfactory way of separating aniline from the other reaction products is by steam distillation. The flask is therefore fitted up with

a steam supply and a condenser as shown in Fig. 43. It is heated while steam is passed so as to maintain brisk boiling. An oily distillate comes over at first, but later appears to consist simply of water. About 100 c.c. of clear water should be collected besides the turbid distillate.

To reduce the amount of aniline in the aqueous layer about 30 gm. of powdered salt are added to the flask containing the distillate, and the mixture is shaken until the salt has dissolved. Using a separating funnel, the upper layer of aniline is then separated and the brine is extracted twice with about 40 c.c. of ether. The aniline and the ether extracts are united and shaken in a conical flask with a little anhydrous potassium carbonate. The liquid is then decanted into a second flask, corked, and left to stand over coarsely powdered potassium hydroxide until it is clear.

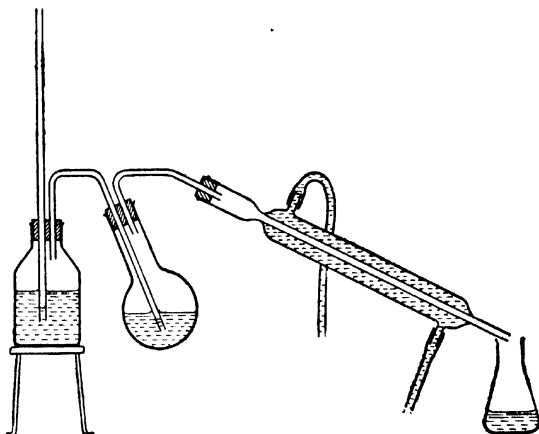


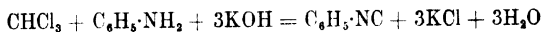
FIG. 43.

The ether must be removed by distillation on the water bath, *following the usual essential precautions* (p. 164). When the water bath has been brought to the boil and no more distillate comes over the water condenser is replaced by an air condenser and the flask is carefully heated with a naked flame. Aniline comes over at 182°–183° C. Yield about 15 gm.

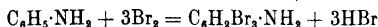
Tests.

1. When one or two drops of aniline are shaken with a little sodium hypochlorite solution or with bleaching powder solution a violet coloration is produced which soon turns brown.

2. On warming a drop of aniline with a few drops of chloroform and about 1 c.c. of alcoholic potash the unpleasant smell of the isocyanide is produced (carbylamine test):



3. When bromine water is added to a solution of a little aniline in fairly strong hydrochloric acid until the brown colour persists, a precipitate of tribrom-aniline is formed :



Note on steam distillation. At the boiling point the sum of the partial pressures of steam (p_1) and aniline (p_2) must be equal to the atmospheric pressure.

$$P = p_1 + p_2$$

It will be seen, from Fig. 44, that the temperature at which steam distillation proceeds must accordingly be less than 100°C . Now the volumes

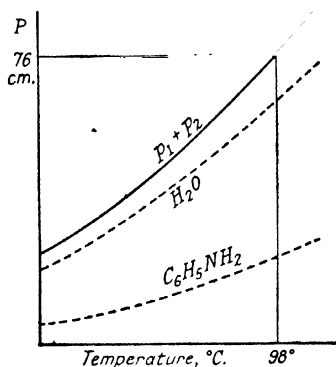


FIG. 44.

in which the vapours are mixed are proportional to the partial pressures. Consequently the weights of water (w_1) and aniline (w_2) are given by :

$$\frac{p_1}{p_2} = \frac{\frac{w_1}{18}}{\frac{w_2}{93}}$$

$$\frac{w_1}{w_2} = \frac{18p_1}{93p_2}$$

The process is therefore more efficient than might be expected.

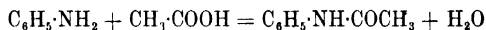
Acetanilide, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{COCH}_3$.

The reactivity of aniline is illustrated by the ready formation of tribrom-aniline (above). The $-\text{NH}_2$ group "activates" the benzene nucleus and makes substitution very easy. Towards many reagents the compound indeed lacks stability and it becomes desirable to protect the

M.P.C.

b

— NH_2 group in particular against attack. Acetylation achieves this and reduces the reactivity of the molecule as a whole.



Required :

25 gm. (25 c.c.) freshly distilled aniline.

30 c.c. glacial acetic acid.

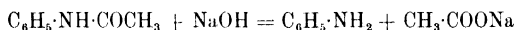
The suitability of the specimen of aniline may be judged from its colour. If very dark it must be redistilled.

The aniline and acetic acid are mixed in a 150 c.c. round-bottomed flask fitted with an air condenser and a thermometer as shown in the figure on p. 179 for the preparation of acetamide. A few pieces of porous earthenware are added and the mixture is boiled on a wire gauze at such a rate that the thermometer reads between 103° and 105° C. After two hours' heating the contents of the flask are poured while hot into 500 c.c. of cold water in a beaker. The white solid which separates is filtered at the pump and washed with a little cold water.

The acetanilide is then dissolved in a 50 per cent. mixture of acetic acid and water (about 100 c.c. should suffice), the solution being made by heating on the water bath. On cooling the substance crystallises out. The crystals are filtered off, washed with a little water and dried in the steam oven. Yield about 30 gm., m.p. 112° C.

Test.

Acetanilide is hydrolysed by boiling with caustic soda solution :



but more rapidly by hot sulphuric acid of about 70 per cent. strength. Free acetic acid and aniline sulphate are formed :

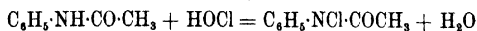


After boiling a little acetanilide with excess of 70 per cent. sulphuric acid under reflux for about 20 minutes some aqueous acetic acid may be removed by distillation. If the residual solution is made alkaline the free amine is liberated and may be submitted to one of the tests given on p. 192.

p-Brom-acetanilide is readily made. About 2 c.c. of bromine are added drop by drop to a solution of 5 gm. acetanilide in a little acetic acid. The appearance of a pale yellow colour indicates a slight excess of bromine. After standing for ten minutes the mixture is poured into water and the precipitate is filtered off and recrystallised from a little alcohol. Both *o*- and *p*-brom-acetanilides are formed, but the latter predominates. Yield 6 gm., m.p. 165° C.

N-chlor-acetanilide, required for the experiment on the law of Mass Action, described on p. 127, is made as follows : 25 gm. of acetanilide are stirred with a solution of 25 gm. potassium bicarbonate in 100 c.c. water

and a thin suspension of 20 gm. bleaching powder in 1 litre of water is added. The exact weight of bleaching powder can only be calculated if the amount of available chlorine in 100 gm. of the solid is determined by one of the volumetric methods given on p. 82 and p. 86. Slightly more than the amount required by the equation



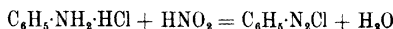
should be used. The mixture should be allowed to stand, with occasional shaking, for about an hour. There is no apparent change in the acetanilide. On shaking the mixture with about 100 c.c. of chloroform the N-chlor-acetanilide is extracted. The bottom layer is run off, using a separating funnel. A second extraction with 50 c.c. chloroform is desirable. The chloroform is removed by distillation on the water bath and the residual liquid, on being poured into a basin, deposits the N-chlor-acetanilide in fair yield. To obtain a purer specimen it should be dissolved in the minimum quantity of hot chloroform and then assisted to separate by adding petroleum ether. m.p. 91°C .

Diazotisation of Aniline. Preparation of compounds from Benzene Diazenium Chloride.

By preliminary conversion into diazonium compounds the aromatic amines can be converted into a variety of important products. The diazonium compounds formed in the presence of acid are salts:



These are strongly dissociated in solution. Since these compounds cannot be kept, it is supposed that enough aniline will be diazotised to carry out these exercises two at a time.



Diazotisation.

Required:

- 15 gm. (15 c.c.) aniline.
- 35 c.c. concentrated hydrochloric acid.
- 11 gm. sodium nitrite.
- Ice.

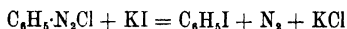
The hydrochloric acid is diluted with 50 c.c. of water, and then the aniline is dissolved in it on stirring. The solution of aniline hydrochloride is placed in a small conical flask cooled in ice and some small pieces of ice are added.

Stirring with a thermometer and seeing that the temperature does not rise above 10° , a solution of 11 gm. sodium nitrite in 50 c.c. of water is run in very gradually. This converts the aniline hydrochloride into benzene diazonium chloride. The solution, kept at between 0° and 10° , is used for the following pairs of experiments.

1. Iodobenzene.

Three-quarters of the solution of diazotised aniline is used for this preparation, 25 gm. of potassium iodide, dissolved in 25 c.c. of water,

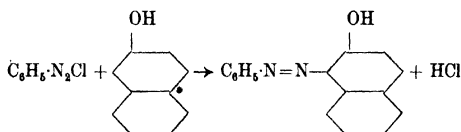
are added to the cold solution and the mixture is well shaken. It is allowed to stand for ten minutes, and then is heated on the water bath for quarter of an hour to complete the reaction. Nitrogen is evolved and some iodine is liberated by the excess of nitrous acid.



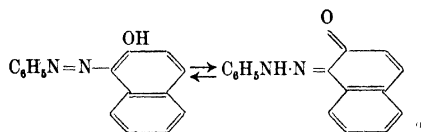
After this time iodobenzene will be seen to have separated as a heavy oil. Bench caustic soda is added until the mixture is alkaline and then the iodobenzene is separated by steam distillation. The apparatus for this is as shown on p. 192. If desired the aqueous distillate can be set aside for treatment on another occasion.

The oil is separated from the water layer, using a separating funnel. If it is dark in colour it may be shaken with a little sodium thiosulphate solution. It is then dried over anhydrous sodium sulphate or calcium chloride and distilled, using an air condenser. The fraction boiling between 185° and 190°C . is collected. The pure liquid boils at 188°C . Yield about 10 gm.

2. Benzene-azo- β -naphthol.



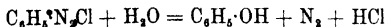
About 1 gm. of β -naphthol is dissolved in about 50 c.c. of bench caustic soda. This solution is then cooled in ice and a cold solution of benzene diazonium chloride is run in. The remainder of the diazotised solution prepared above will be required. It must be noted that the diazotised aniline is run into the phenol solution and not *vice versa*. A scarlet precipitate of benzene-azo- β -naphthol is formed. This is filtered off and washed with water on the filter. It is difficult to crystallise, and when moist is not readily soluble in acetic acid from which, however, it can be recrystallised. About 1 gm. of the crude product should be obtained. It is insoluble in caustic soda, and for this reason the formula given above must be inaccurate. There appears to be a transformation represented by :



the second formula being perhaps a better representation of the product.

To prepare the next two compounds a second quantity of aniline (15 gm.) should be diazotised as described above.

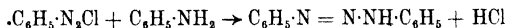
3. Phenol from Benzene Diazonium Chloride.



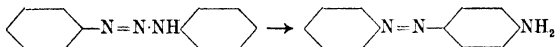
Half the diazotised aniline solution prepared above is allowed to stand in a flask at room temperature for about quarter of an hour. This ensures complete diazotisation. The flask containing the solution is warmed in a water bath at about 50° for half an hour. The temperature of the solution should not exceed 55° C. Nitrogen is given off briskly and the solution darkens in colour. The smell of phenol becomes noticeable. The phenol may be extracted with ether and the ether extract dried over calcium chloride. On distilling off the ether, taking the usual precautions, a residue of impure phenol is obtained. The substance can be identified by the tests given on p. 200. Phenol can be distilled, using an air condenser, at 175°–185°. Yield about 6 gm., m.p. 41° C.

4. Diazoamino-benzene.

To the remaining half of the diazotised aniline solution 7 c.c. of aniline are added, and the mixture is vigorously stirred. Diazoamino-benzene separates as a yellow crystalline precipitate :



This substance may be filtered off and recrystallised from alcohol, m.p. 98° C. Yield about 7 gm. On heating with aniline hydrochloride or on treatment with excess mineral acid the compound undergoes an important transformation into amino-azo-benzene :



p-amino-azo-benzene is usually formed, but if the para position is occupied a derivative of the ortho compound is formed.

The Reactions of Primary, Secondary and Tertiary Amines. *

The reactions to be described are the following :

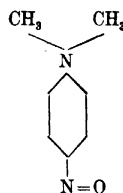
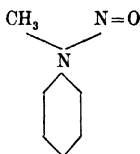
- (i) The carbylamine (Hofmann) reaction of primary amines.
- (ii) The reaction with nitrous acid.
- (iii) The reaction with benzene sulphonic chloride (Hinsberg's method of separating primary, secondary and tertiary amines).

These are general reactions which are used in distinguishing these three types of compound, whether aliphatic or aromatic. The reaction of aniline with carbon disulphide and of dimethylaniline with ethyl iodide are also of interest.

(i) On warming a drop of aniline with a few drops of chloroform and about 1 c.c. of alcoholic potash the unpleasant smell of phenyl isocyanide is produced. This is a general reaction of all primary amines. The presence of acidic groups interferes, however, since the isocyanide is retained by the alkaline solution and is not volatile. Secondary and tertiary amines do not produce isocyanides.

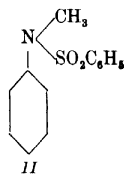
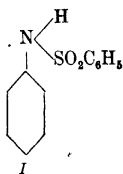
Tests (ii) and (iii) should be carried out on aniline, methylaniline and dimethylaniline.

(ii) About 1 c.c. of each of the three amines is dissolved in excess of dilute hydrochloric acid and the solution is cooled to $0-10^{\circ}\text{C}$. Sodium nitrite solution is then added slowly to the stirred solution until a drop of the mixture turns starch iodide paper blue. This indicates an excess of nitrous acid. On heating the solution nitrogen is produced and there is a smell of phenol. With methylaniline and dimethylaniline, nitroso-compounds are formed :



The first of these compounds separates as a yellow oil, but it is very desirable to extract it with ether and to wash the ether extract with water. The residue left after evaporating the ether may be subjected to Libermann's nitroso reaction (p. 200). The *p*-nitroso-compound derived from dimethylaniline separates as the yellow hydrochloride. On treating this with caustic soda the green base is liberated.

(iii) To 5 c.c. of 10 per cent. caustic soda solution in a test tube 4 drops of the amine are added, followed by 7 or 8 drops of benzene sulphonie chloride. The mixture is shaken for five minutes and then it is heated gently and again shaken. Aniline gives the alkali-soluble sulphonamide I, methylaniline gives the sulphonamide II, which is not soluble in alkali.



Dimethylaniline does not react. II separates from the alkaline mixture. I is precipitated by adding a little bench hydrochloric acid.

Note. Benzoyl chloride can be employed here, but the products are not easily separated.

Sulphanilic Acid.



Concentrated sulphuric acid is a sulphonating agent. It is much used for introducing the sulphonic acid group, $-\text{SO}_3\text{H}$, on to the benzene nucleus: $\text{C}_6\text{H}_6 + \text{HO-SO}_3\text{H} = \text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O}$

Fuming sulphuric acid and chlorosulphonic acid, ClSO_3H are more rapid in their action. The reaction with aniline might be expected to be rapid owing to the presence of an "activating" group. In the presence of excess sulphuric acid this is not so since the properties of the $-\text{NH}_2$ are greatly altered by salt-formation.

Required :

26 gm. (25 c.c.) aniline.

80 gm. (45 c.c.) concentrated sulphuric acid.

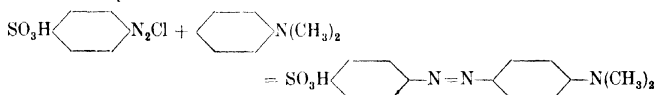
The aniline is placed in a 250 c.c. round-bottomed flask, and the sulphuric acid is added gradually with frequent shaking of the mixture. The flask is then heated at 180° – 190° C. on an oil bath or metal bath* for a total of four or five hours. At the end of this time a sample of the mixture when dissolved in a little water in a test tube remains clear when made alkaline with caustic soda. If oily drops of aniline separate the reaction is not complete.

On pouring the mixture into 200 c.c. of cold water sulphanilic acid separates as a grey solid. This is filtered off, washed with cold water and recrystallised from hot water with the use of 4 or 5 gm. of animal charcoal. It is dried in the steam oven. Yield about 25 gm. It has no melting point but decomposes on heating to a high temperature.

Note. It will be noted that only the *p*-sulphonic acid is isolated from this experiment. The *o*-compound is formed in only small quantities, and separation is effected in the recrystallisation.

Preparation of Methyl Orange.

This compound may be made by coupling diazotised sulphanilic acid with dimethylaniline.

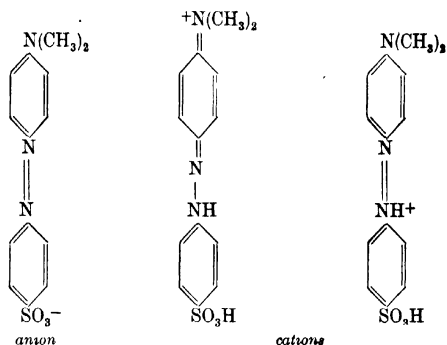


Coupling takes place at the very reactive *p* position of dimethylaniline.

2.5 gm. anhydrous sodium carbonate are dissolved in 100 c.c. of water and 10 gm. sulphanilic acid are added. The acid dissolves on stirring and warming. 3.5 gm. of sodium nitrite in 20 c.c. of water are added and the mixture is cooled in ice. A solution of 6 c.c. of concentrated hydrochloric acid in 10 c.c. of water is then run in gradually. This diazotises the sulphanilic acid, which must be kept cold. On adding a solution of 6 gm. dimethyl aniline in 6 c.c. of concentrated hydrochloric acid and 20 c.c. water the azo compound is formed. Addition of caustic soda until the mixture is alkaline causes the separation of the sodium compound of the compound represented in the formula. This is methyl orange. It is filtered off and washed with water and dried. It can be recrystallised from hot water. Yield about 12 gm.

* A mixture of one part lead to two parts bismuth. This is fluid above 120° ; above 140° most oils fume badly.

Note. In alkaline solution methyl orange has the orange colour of the anion. In acid solution it is red. The deepening of the colour has been ascribed to "resonance" between the two cations shown below.



Reactions of Phenol.



Phenol is much more reactive than benzene itself. The presence of amino or hydroxyl groups directly attached to the ring greatly enhances the reactivity of the benzene nucleus, especially at the carbon atoms which are ortho and para in respect of the activating group. The stability of the ring itself is reduced, and it can be much more readily ruptured by oxidising agents.

1. Liebermann Nitroso Reaction. In a clean dry test tube about 0.5 gm. of phenol is heated with a very small crystal of sodium nitrite, so that the mixture is just melted to a homogeneous condition. The molten substance is allowed to cool, and then twice its volume of concentrated sulphuric acid is added. On rotating the tube slowly in order to mix the contents a deep green or blue coloration slowly develops. On adding an equal volume of water the solution turns red or reddish-brown. Excess caustic soda turns it blue or purple.

This is a good test for phenols provided the para position is not occupied. The explanation seems to be that *p*-nitroso phenol is formed and then condensation with more phenol takes place.

N.B.—The test can be carried out with a *N*-nitroso compound instead of sodium nitrite. It is thus a test for these compounds (p. 198).

2. Schotten-Baumann Reaction. This is a reaction for the benzylation of phenols (and primary or secondary amines):—



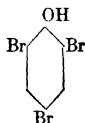
5 gm. of phenol are dissolved in about 60 c.c. of bench caustic soda contained in a wide-necked bottle or conical flask of about 200 c.c. capacity.

10 c.c. of benzoyl chloride are then added and the mixture is shaken vigorously for ten to fifteen minutes. Care should be taken not to get benzoyl chloride, even in the presence of alkali, on the hands.

The solid ester, phenyl benzoate separates and is filtered off at the pump. It should be thoroughly washed with water and then recrystallised from methyl or ethyl alcohol. Yield about 8 gm., m.p. 69°.

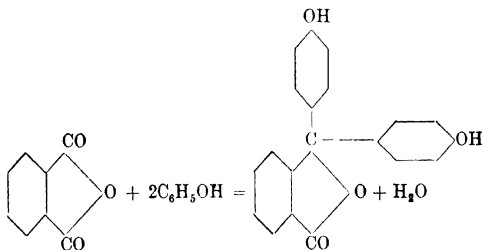
The experimental procedure for benzoylating aniline is exactly similar. Benzanilide, m.p. 163°.

3. Tribromophenol.

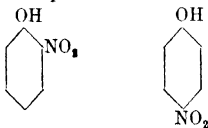


1 or 2 gm. of phenol are dissolved in about 50 c.c. of water in a beaker and then bromine water is run in until there is an excess (about 300 c.c. is required). At first the bromine water is decolorised, but finally a white or very pale yellow precipitate of tribromophenol is formed. It may be recrystallised from aqueous alcohol or aqueous acetic acid; m.p. 95° C.

4. Phenolphthalein (Phthalein reaction). About 1 gm. of phenol is mixed with an equal quantity of phthalic anhydride and moistened with two or three drops of concentrated sulphuric acid. The mixture is then gently fused for about a minute. After cooling a little excess caustic soda is added. A bright red coloration results.



o-Nitrophenol and *p*-Nitrophenol.



The nitration of phenol itself tends to go rapidly even in a solvent such as acetic acid, and the main product is 2-4-dinitrophenol. *o*- and *p*-nitrophenol are not made very satisfactorily by the action of nitric and sulphuric acids. Some of the phenol is oxidised with rupture of the ring, and condensation between the various substances then present is the probable source of the resinous, non-crystallisable, products.

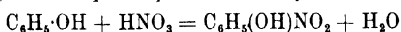
Required :

- 80 gm. sodium nitrate or 95 gm. potassium nitrate.
 100 gm. (55 c.c.) concentrated sulphuric acid.
 50 gm. phenol.

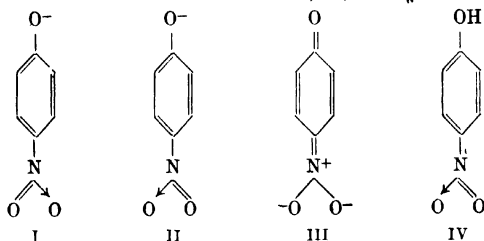
The nitrate is dissolved on warming with 200 c.c. of water in a litre flat-bottomed flask. Before the solution is quite cool the sulphuric acid is added and the mixture is stirred and cooled to about 20° C. At this temperature a mixture of 5 c.c. of water and 50 gm. of phenol, warmed so that the latter forms a liquid with the water, is added drop by drop from a tap funnel. The nitrating mixture must be well shaken during this addition and its temperature must be maintained between 20° and 25°. The contents of the flask are then allowed to stand for about an hour.

About 400 c.c. of water are then added. This causes the separation of a heavy oil. The aqueous layer is decanted as far as possible and the oil is washed by decantation with water so as to free it from acid. It is then subjected to steam distillation (p. 192) in order to separate the *o*- and *p*-nitrophenols. Of two such isomers the ortho form always has the lower m.p. and b.p. A good yield of the *o*-nitrophenol comes over and solidifies. If it solidifies in the Liebig condenser the water flow can be turned off until the solid melts and is carried through (m.p. 45°). The *o*-nitrophenol is filtered off and recrystallised from aqueous alcohol. Yield about 30 gm.

The extraction of the *p*-nitrophenol from the resinous material in the flask is best effected by adding a little concentrated hydrochloric acid and about 10 gm. of animal charcoal. The mixture is then boiled on a wire gauze with gentle shaking to prevent the resin sticking. The mixture is then filtered hot through a double thickness of filter paper into a filter flask, which contains some warm water (to prevent cracking). On cooling, the filtrate may deposit the yellow *p*-nitrophenol, but if an oil separates it must be subjected to a second charcoal treatment and filtration. Not more than 5 gm. of the *p*-nitrophenol is usually obtained; m.p. 114° C.



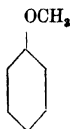
Note. The more polar character of *p*-nitrophenol is discussed by Speakman (*Valency*, p. 99). Both these phenols (and *m*-nitrophenol) give red solutions in alkali. This has been attributed to "resonance" among the different forms for the anion I, II, III : ,



When thoroughly dried the covalent form IV (obtained from acid solutions) is colourless. As ordinarily made all the nitrophenols are yellow.

The nitrophenols show a more marked acidic character than phenol itself and will, for example, decompose sodium carbonate solution on warming.

Anisole.



An example of methylation using dimethyl sulphate. (*N.B.* The vapour of dimethyl sulphate is exceedingly poisonous.)

Required :

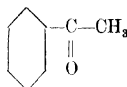
- 19 gm. phenol
- 10 gm. caustic soda in 70 c.c. of water
- 24 c.c. dimethyl sulphate.

The phenol is dissolved in the caustic soda in a round 250 c.c. flask. The dimethyl sulphate is then added, about 5 c.c. at a time, with vigorous shaking. There is a rise in temperature and the temperature should not rise above 60°. When the mixture begins to cool it is heated on the water bath for ten minutes and then the upper oily layer of anisole is separated, using a funnel. It is washed with a little water, dried over calcium chloride and distilled. Yield 17 gm., b.p. 150°–152° C.

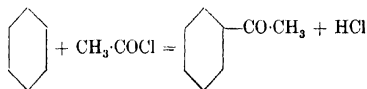


Using diethyl sulphate instead of dimethyl sulphate the ethyl ether, phenetole, may be made b.p. 172° C. The conversion of such compounds back to the parent phenol is carried out by refluxing with hydriodic acid.

Acetophenone.



This compound, and others like it, may be made by a modification of Friedel and Craft's reaction. Benzene is treated with acetyl chloride in the presence of freshly prepared aluminium chloride.



Required :

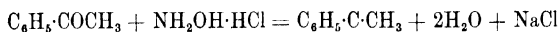
- 30 gm. (37 c.c.) dry benzene.
- 36 gm. (35 c.c.) acetyl chloride.
- 50 gm. aluminium chloride.

The specimen of aluminium chloride should be either freshly made or

taken from a sealed glass container freshly opened. The aluminium chloride and benzene are mixed in a 250 c.c. round-bottomed flask fitted with a reflux condenser and set up in the fume chamber. The flask is kept cool by cold water, while the acetyl chloride is run slowly down the condenser from a tap funnel. The flask should be shaken at intervals. It is then advisable to allow the reaction to go to completion by placing the flask in a water bath at about 40°–50° C. The contents of the flask are converted into a brown viscous mass, which is then shaken into a large beaker containing about 200 c.c. of cold water. The mixture is thoroughly stirred. A dark oil separates on the surface. To extract the acetophenone the mixture is extracted with benzene. 50 c.c. of benzene are added, and the mixture is shaken in a large separating funnel. The benzene layer is separated and is then shaken with some dilute caustic soda and then with water. It is finally dried over anhydrous calcium chloride and distilled. After the benzene has come over, an air condenser is substituted and the acetophenone distils at 195°–202° C. This is collected in a separate receiver. Yield about 20 gm. The pure ketone boils at 202° C. and solidifies in cold weather; m.p. 20° C.

Note. Acetophenone contains a somewhat reactive methyl group. It is readily brominated to give ω -brom-acetophenone, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\text{Br}$, and it condenses with benzaldehyde to give chalkone.

Acetophenone-oxime. $\text{C}_6\text{H}_5\text{—C—CH}_3$.



*5 gm. of hydroxylamine hydrochloride are dissolved in 10 c.c. of water and 8 c.c. of acetophenone are added. 3 gm. caustic soda dissolved in very little water are then added. Enough alcohol is then added to give a clear solution when hot. The mixture is boiled on the water bath for two hours and poured into about 100 c.c. of cold water. The oxime is then extracted with ether and the residue, obtained after distilling off the ether, is recrystallised from petroleum ether. Yield about 8 gm., m.p. 58°–60° C.

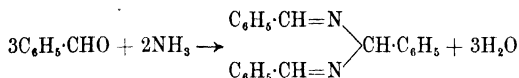
Reactions of Benzaldehyde.



Tests 1, 3 and 4 for (aqueous) acetaldehyde on p. 168 may be carried out on benzaldehyde. The reactions are more difficult in this case. Benzaldehyde also gives a bisulphite compound in the manner described on p. 169 for acetaldehyde. The reactions of benzaldehyde with caustic

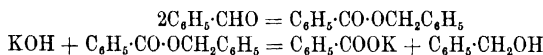
soda and with ammonia, are, however, different, and formaldehyde alone among the common aliphatic aldehydes resembles the compound in some respects.

1. Hydrobenzamide. Water is eliminated between two molecules of ammonia and three molecules of benzaldehyde:



5 c.c. of concentrated ammonia solution (sp. gr. 0.88) are added to 1 c.c. of benzaldehyde in a stout test tube. The tube is then securely corked and the mixture is vigorously shaken and then left to stand for at least twenty-four hours. The aldehyde is converted into a hard solid mass. If not quite solid at the end of this period the mixture must be shaken and left for a further period. The hydrobenzamide is then broken up and recrystallised from a little absolute alcohol; m.p. 101°C . The substance is very readily hydrolysed back to its components.

2. Benzoic acid and Benzyl alcohol (Cannizzaro's Reaction). In the presence of concentrated KOH (or NaOH) benzaldehyde undergoes a reaction whereby benzyl alcohol and potassium benzoate are formed in equimolecular quantities. Benzyl benzoate is probably intermediate:



9 gm. of caustic potash are dissolved in 6 c.c. of water (or 7 gm. caustic soda in 8 c.c.) and, when cold, 10 c.c. of benzaldehyde are added. This mixture is shaken in a small conical flask which is set aside when a permanent emulsion has been formed. After three or four hours a dense solid mass is formed. About 30 c.c. of water are needed to dissolve the solid matter present, and the mixture may require to be warmed. If so, it must be cooled to room temperature before extracting the benzyl alcohol with ether. This leaves the potassium or sodium benzoate in the aqueous layer. Evaporation of the ether leaves benzyl alcohol (contaminated with a little benzaldehyde); the benzoic acid is easily obtained by adding dilute hydrochloric acid to the aqueous solution. Benzyl alcohol distils at $200^\circ\text{--}207^\circ$. Benzoic acid melts at 121° . It may be recrystallised from hot water.

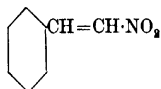
3. Benzaldehyde phenylhydrazone. The phenylhydrazone may be made without great difficulty, and there is no need to use 2-4-dinitrophenylhydrazine in place of ordinary phenylhydrazine. Nevertheless, the 2-4-dinitro compound is exceedingly well crystallised and its preparation may be preferred. The method is exactly similar.



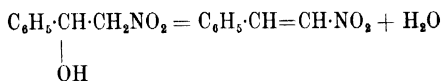
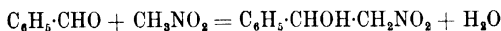
3 c.c. of benzaldehyde and 6 c.c. of phenylhydrazine are separately dissolved in 10 c.c. quantities of glacial acetic acid (11 gm. of 2-4-dinitro-

phenylhydrazine would be needed, and 20 c.c. of acetic acid). The phenylhydrazine solution is diluted with an equal volume of water, and then the two solutions are mixed in a conical flask. On shaking, the phenylhydrazone soon separates, and after five minutes it is filtered at the pump and washed with a little 50 per cent. acetic acid. It is recrystallised from a little alcohol. Yield about 5 gm. pale yellow needles; m.p. 158°. The 2,4-dinitrophenylhydrazine is obtained in the form of red needles; m.p. 243°.

***ω*-Nitrostyrene.**



This preparation is included, since it is a good illustration of an important condensation: that which takes place between the aldehydic group of an aromatic aldehyde and a reactive methyl or methylene group. (Cf. condensation of benzaldehyde with acetone and with acetic acid.)



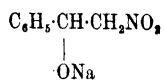
Required:

- 15 gm. (13 c.c.) nitromethane (p. 183).
- 26.5 gm. (25 c.c.) benzaldehyde.
- 50 c.c. methyl alcohol.
- 10 gm. caustic soda in 25 c.c. water.
- Ice.

The nitromethane, benzaldehyde and methyl alcohol are mixed in a flat-bottomed flask standing in a mixture of ice and salt. The caustic soda solution is cooled with ice, and then a little of it is run in from a tap funnel. There is a "period of induction" and then heat is evolved. The temperature must be kept between 10° and 15°, so ice is added to the mixture when necessary. After the first small quantity of alkali has been added the remainder may be added rather more rapidly. At this stage a sodium derivative of the intermediate hydroxy-compound is formed and may separate out. A further 10 c.c. of methyl alcohol may be added to redissolve it.

After standing for 10 minutes, 300 c.c. of ice-water, containing a little solid ice, are added. Then, when the temperature is below 5°, the alkaline solution is run into a solution of 100 c.c. of concentrated hydrochloric acid in 150 c.c. of water. The nitrostyrene separates as a pale yellow solid. It is filtered, washed at the pump with water and recrystallised from a little alcohol. Yield about 20 gm. yellow needles; m.p. 58° C.

Note. The sodio-derivative formed intermediate may be represented by the formula :



Nitrostyrene has the properties of an unsaturated compound owing to the olefine side-chain.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

All organic compounds contain carbon, but not necessarily hydrogen. If it is desired to test for the presence of carbon in a substance the test for hydrogen may conveniently be carried out at the same time.

Carbon and Hydrogen.

The substance is oxidised by heating it with pure copper oxide. The copper oxide must first be heated strongly in a crucible to drive off adsorbed water.

An intimate mixture of about 0.5 gm. of the powdered substance and about 5 gm. of the copper oxide is heated in a clean dry test tube, fitted with a short delivery tube (Fig. 45).

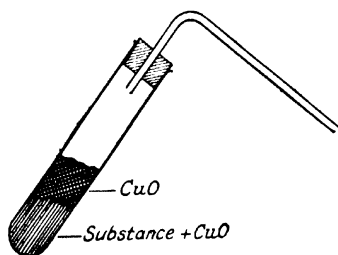


FIG. 45.

If the delivery tube dips into lime water the presence of carbon is indicated by a white precipitate due to carbon dioxide. If sulphur is known to be present (below) the gas must be bubbled through a little potassium dichromate in sulphuric acid in a test tube and then into lime water.

The presence of hydrogen is indicated by the condensation of water on the upper part of the test tube. Water can be recognised

by its action on anhydrous copper sulphate which turns from white to blue.

Halogen. (Beilstein test).

A small square of medium mesh copper gauze is held in the tongs and heated in a Bunsen flame to dull redness until any initial green coloration has passed. When the gauze is somewhat cooled a little of the powdered organic compound is placed on the spot previously heated, and then the gauze is reheated in the outer part of the flame. Immediately succeeding the luminosity due to the combustion of an inflammable compound, there is a transient bright green coloration if halogen is present. This is due to the volatilisation of copper halide formed by the action of hot copper oxide on the halogen compound.

This is a reliable *negative* test, but if a positive result is obtained halogen should be confirmed by performing the Lassaigne or Middleton fusion given below. The reason for this is that certain amides, containing no halogen, can cause the green coloration through the formation of copper cyanide.

Nitrogen, Sulphur and Halogen by the Lassaigne Fusion.

This test, invented by Lassaigne, enables one to test for the presence of nitrogen, sulphur and halogen. It must not be performed in the case

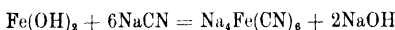
QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS 209

of compounds which decompose violently on heating nor with carbon tetrachloride or chloroform, since violent explosions may result. A safer test is Middleton's fusion given below.

About 0.5 gm. of the *dry* substance is melted in an ignition tube or a small hard glass test tube, with a small piece of sodium about half the size of a pea. This quantity of sodium must not be exceeded. The tube is held in the tongs and pointed away from the experimenter or anyone else in the vicinity. It is then heated very gently until any initial reaction has subsided and no more fumes are seen. It is then safe to heat the tube to dull redness. It is then immediately lowered in a vertical position into about 20 c.c. of distilled water in a small clean mortar. The tube disintegrates and the water reacts vigorously with the residue of sodium peroxide and a little sodium. It is advisable to tap the tube firmly on the bottom of the mortar so as to distribute and cool the contents. This reduces the risk of the contents being blown into the air through formation of steam.

The mixture in the mortar is stirred and powdered with the pestle. It is then filtered. The filtrate is divided into three parts, which are treated as described below.

1. Test for Nitrogen. If nitrogen is present it will have formed sodium cyanide. An equal volume of freshly made ferrous sulphate solution is added. If a dark greenish-grey precipitate of ferrous hydroxide does not form, a little caustic soda solution is added. The mixture is then boiled in a boiling tube for a few minutes so that potassium ferrocyanide may be formed:



The solution is then acidified. A dark blue colour at this stage indicates nitrogen, there being enough ferric salt formed by oxidation to give the precipitate of Prussian blue. Otherwise ferric chloride is added after acidifying. Nitrogen is indicated by a dark blue coloration or precipitate.

If a green coloration is obtained it may be due to insufficient reaction with sodium in the original fusion. This is a difficulty which arises with volatile compounds. If the fusion is repeated it may be advantageous to add the substance in small quantities to some molten sodium in an ignition tube. That is, the order of the substances is reversed.

2. Test for Sulphur. If sulphur is present it will have formed sodium sulphide. Mix the second portion of filtrate with an equal volume of *freshly made* sodium nitroprusside solution. A bright violet or purple colour indicates sulphur.

Sodium nitroprusside has the formula $\text{Na}_2[\text{Fe(CN)}_5\text{NO}]$. The purple compound is represented by $\text{Na}_4[\text{Fe(CN)}_5(\text{NOS})]$.

3. Test for Halogen. If the Beilstein test gives a positive result halogen may be present. If so, a sodium halide will be formed during the Lassaigne fusion. The procedure depends on whether nitrogen has been shown to be present.

M.P.C.

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(a) Nitrogen absent : the filtrate is acidified with dilute nitric acid and silver nitrate solution is added :

White ppt. soluble in NH_4OH *chloride.*

White ppt. slightly soluble in NH_4OH *bromide.*

Pale yellow ppt. insoluble in NH_4OH *iodide.*

(b) Nitrogen present : the filtrate is acidified with dilute nitric acid and evaporated in a basin (in the fume chamber) to half the original volume. This is necessary to drive off the cyanide as hydrocyanic acid (exceedingly poisonous). After the evaporation silver nitrate is added as in (a).

Middleton's Method. This method has an advantage over the Lassaigne method, in that the reaction is less violent and there is no excess sodium to be disposed of. Pure zinc dust and anhydrous sodium carbonate are used instead of sodium. Any sulphur present forms insoluble zinc sulphide ; halides and cyanides are detected in the same manner as before.

About 1 gm. of zinc dust (A.R. standard) is mixed with about half its weight of anhydrous sodium carbonate, and the mixture is then placed in an ignition tube. A quantity of the organic compound which represents about a fifth of the zinc-carbonate mixture is then added and thoroughly mixed. A 1-inch layer of the zinc-carbonate reagent is then introduced into the tube and pressed firmly with a glass rod. When heating, the flame is first applied near the top of the mixture and then the heating is gradually extended until the whole of the contents are heated to redness. The heating is continued for about two minutes, and then the hot tube is plunged into 20 c.c. of distilled water in a clean mortar. The mixture is well ground with a pestle and then transferred to a beaker and boiled for a few seconds. The clear solution is then decanted into a filter. The tests to be applied to the filtrate are as in 1 and 3 above for the Lassaigne fusion.

To test the residue on the filter paper for sulphide it is simply necessary to add about 10 c.c. of dilute hydrochloric acid and test for hydrogen sulphide. This is best done by placing over the filter a filter paper in the centre of which a drop of lead acetate solution is placed. A black coloration indicates the presence of sulphur in the original substance.

Metals.

The presence of a metal in an organic compound is detected by igniting a little of the substance on a crucible lid until all black carbonaceous matter is burnt away. A white residue is left by alkali metals (carbonates) and by alkaline earths (oxides). A flame test may be helpful. The recognition of the metal may require the examination of the residue by the methods of qualitative analysis.

THE RECOGNITION OF SIMPLE ORGANIC COMPOUNDS

The identification of organic compounds other than those of comparatively simple nature lies beyond the beginner in organic chemistry.

The following is therefore a simple introduction to the subject only. The tests described should preferably be performed after the elements present in the compound have been discovered (p. 208) for this information may immediately exclude certain classes of compound as possibilities.

A. Preliminary tests are carried out so as to discover, if possible, the kind of compound the substance is, e.g. alcohol, aldehyde, ester, etc.

I. Action of water (cold then warm). The compound may prove to be
(a) an insoluble solid or immiscible liquid :

e.g. hydrocarbons and their halogen-substituted derivatives,
most ketones, ethers and esters, amines,
most cyanides or nitriles,
nitrocompounds,
aromatic aldehydes,
(some aromatic acids and phenols are sparingly soluble and may crystallise out on cooling the hot solution).

If the substance is not perceptibly soluble it is advisable immediately to try :

(i) dilute HCl. If this causes the substance to dissolve up it is probably an amine. An acetyl derivative may be prepared from a primary or secondary amine (p. 178, test 3) and its melting point found.

(ii) dilute NaOH. This in the cold dissolves acids and phenols, also some esters.

(b) a soluble solid or a readily miscible liquid :

e.g. common alcohols,
phenols,
aliphatic aldehydes,
acetone,
low molecular weight amides and urea,
carboxy acids and their sodium, potassium and ammonium salts,
sugars,
low molecular weight aliphatic amines,
methyl oxalate.

The solution in water should be tested with litmus. Salts of organic acids are commonly slightly alkaline ; salts of organic bases and strong acids are commonly slightly acidic. In either case, to gain further information, samples of the solution should be

(i) made acid with dilute H_2SO_4 . This will liberate the free acid from its salt. The acid may be recognisable by its smell (warm) or because it is obtained in the form of a white precipitate which can be filtered off, washed, dried and then the m.p. found.

(ii) made alkaline with 30% NaOH and warmed. A strong ammoniacal, fishy smell will indicate an aliphatic amine (the

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vapour may ignite). Aromatic amines will be liberated from their salts in the form of oily drops or as a suspension. The free base may then, in the latter case, be isolated and acetylated to obtain a solid derivative (p. 178, test 3).

Amides liberate ammonia and the sodium salt of the corresponding acid is formed. On acidifying with dilute H_2SO_4 the acid is liberated (smell, or note precipitate).

Chloral reacts with alkali to give chloroform (smell.)

(c) a liquid or a solid which, although not miscible (or soluble) in water, in the cold or on warming undergoes hydrolysis.

e.g. acid anhydrides, acid chlorides.

In these cases a strongly acid solution will be formed as the reaction proceeds. Acid chlorides liberate chloride ion which may be recognised by testing with silver nitrate and dilute nitric acid.

II. If the action of caustic soda has not been examined under I (b) above the test should now be carried out. (Use 30% solution.)

Acids and phenols dissolve in cold NaOH ,

Ammonium salts give a smell of ammonia without heating.

Amides give ammonia only on heating.

Esters are slowly hydrolysed on heating (the change being observed when the mixture is boiled under reflux for some minutes).

The sodium salt of the acid may separate out.

Volatile amines are liberated from their salts. (These smell of ammonia as well as having a fishy smell and the vapour is inflammable).

Aliphatic aldehydes gives brown resins; aromatic aldehydes undergo the Cannizzaro reaction and deposit a white solid (the sodium salt of the acid formed).

III. If the substance is much more readily soluble in caustic soda than in water, it should be treated with cold sodium carbonate solution. The mixture may be gently warmed if there is no visible action in the cold. Carbon dioxide is evolved when acids, nitro- or chloro-phenols, or polyhydric phenols are present.

IV. Bromine in carbon tetrachloride is used as a test for unsaturation. The reagent is added to a solution of the substance in carbon tetrachloride, chloroform or petrol ether. It can be added direct to a liquid compound. Instant decolorisation of each drop of bromine solution as it goes in, without the evolution of HBr indicates unsaturation. If HBr is evolved (acid fumes) substitution is taking place (aliphatic aldehydes, ketones and acid chlorides are readily substituted). Some phenols and aromatic amines give precipitates.

V. Baeyer's Reagent (p. 167). The purple colour is destroyed by unsaturated compounds, aldehydes and formic acid, and phenols. Acetone and methyl ethyl ketone do the same on warming.

VI. Organic acids or their sodium salts should be powdered with soda lime and heated in a dry test tube. The volatile product may be recognised from its smell, the way in which it burns, etc.

Formic or oxalic acid gives hydrogen ;

Acetic acid gives methane ;

Benzoic acid gives benzene ;

Tartaric or citric acid gives a smell of burnt sugar ;

Glycine gives methylamine (alkaline, fishy smell and inflammable.)

B. The **boiling point** or **melting point** of the substance should be found. A small scale distillation is much the best way of examining an unknown liquid to determine its boiling point. It may prove to be a mixture. The following table gives the b.p. and m.p. of some of the commoner compounds.

Hydrocarbons		b.p. (° C.)	m.p. (° C.)
	Benzene	80	5.5
	Toluene	110	
	o-Xylene	142	
	Naphthalene		80
Halogen-substituted hydrocarbons	Methyl iodide	43	
	Ethyl bromide	38	
	Ethyl iodide	72	
	n-Propyl iodide	102	
	iso-Propyl iodide	89	
	Ethylene dichloride	84	
	Ethylidene dichloride	58	
	Ethylidene dibromide	109	
	Chloroform	61	
	Carbon tetrachloride	76	
	Iodoform		119
	Benzyl chloride	176	
Alcohols	Methyl alcohol	65	
	Ethyl alcohol	78	
	n-Propyl alcohol	97	
	Benzyl alcohol	205	
Esters	Methyl acetate	57	
	Ethyl acetate	77	
	Methyl benzoate	199	
	Ethyl benzoate	212	
	Methyl oxalate	163	54
	Ethyl oxalate	186	
	Phenyl benzoate		69
Aldehydes	Acetaldehyde	21	
	Paraldehyde	124	
	Metalddehyde		112 (sublimes)
	Metaformaldehyde		171
	Chloral	96	
	Chloral hydrate		57
	Benzaldehyde	179	

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Sugars		b.p. (° C.)	m.p. (° C.)
	Glucose		144
	„ osazone		210
	Fructose		95
	„ osazone		210
	Galactose		163
	„ osazone		184
	Lactose		203
	„ osazone		200
Ketones			
	Acetone	56	
	Methyl ethyl ketone	81	
	Acetophenone	202	26
	Benzophenone		48
Amines			
	Aniline	183	
	acetyl derivative		112
	Methyl aniline	192	
	acetyl derivative		102
	Dimethyl aniline	193	
Amides			
	Acetamide		82
	Benzamide		128
	Urea		132
	Oxamide		Decomp.
Carboxy-acids			
	Formic	101	
	Acetic	118	
	Propionic	141	
	Chloracetic		63
	Oxalic		98
	Benzoic		121
	Cinnamic		133
	Salicylic		155
Acid chlorides and anhydrides			
	Acetyl chloride	55	
	Acetic anhydride	136	
	Benzoyl chloride	198	
Phenols			
	Phenol	183	41
	Resorcinol	277	110
	Quinol		169
	o-Nitrophenol		44
	p-Nitrophenol		114
Ethers			
	Diethyl ether	35	
	Anisole	152	
	Phenetole	172	
Nitro-compounds			
	Nitrobenzene.	210	
	m-Dinitrobenzene.		90
	o-Nitrophenol		45
	p-Nitrophenol		114

C. To confirm that the compound has been correctly identified it is highly desirable—especially in the case of a liquid—to prepare from it a

crystalline derivative and determine its melting point. The following are suggestions of methods of procedure which might be followed.

1. Aromatic hydrocarbons may be converted to solid nitro-compounds by the action of nitric acid under carefully regulated conditions. Thus benzene yields *m*-dinitrobenzene m.p. 90°C . It is, however, *highly dangerous for a beginner to attempt to nitrate a substance about the identity of which there is any doubt*. Such an experiment should be done only under instructions. An alternative is to attempt to crystallise a picrate by mixing warm alcoholic solutions of the substance and picric acid, e.g. naphthalene picrate (a molecular compound) m.p. 149°C .
2. From alcohols or phenols attempt to prepare the benzoyl ester by the Schotten Baumann method (p. 200). This is most suitable when the ester proves to be a solid for it can then be filtered off and recrystallised.
3. From aldehydes and ketones the phenylhydrazone or 2-4-dinitrophenylhydrazone may be made following the procedure described on p. 170.
4. Amines (primary and secondary) may be converted into their acetyl or benzoyl derivatives (pp. 178 and 201). Picrates of many organic bases are readily obtained by adding a solution of picric acid in alcohol to a solution of the free base. In the case of aniline it is best to use aniline hydrochloride in water and sodium picrate solution. Aniline picrate m.p. 181° , dimethyl aniline picrate m.p. 142° .
5. Amides of aromatic acids may be hydrolysed by heating with a little 30% caustic soda. The solution is then diluted and made acid with hydrochloric acid. This precipitates the organic acid which may be filtered off and recrystallised, probably from hot water. Urea alone of common amides readily gives a crystalline nitrate on adding a little conc. HNO_3 to the solution in water.
6. Acid chlorides and esters may be readily converted into amides, which are crystalline bodies, by suitable treatment with ammonia. Cf. p. 180, the preparation of oxamide and benzamide.
7. Aromatic amines and phenols and some of their derivatives readily give crystalline brom-substituted compounds when treated in solution with bromine water, cf. pp. 193, 201.

It is frequently necessary to transform the substance into a different one which may be more certainly recognised. Thus nitro-compounds are reduced to primary amines by the action of zinc dust in acetic acid—the mixture finally being made alkaline to liberate the base. Cyanides may be hydrolysed by refluxing with caustic soda until no more ammonia is evolved; a solution of the sodium salt of the corresponding acid is then obtained and from this the free acid may be liberated. In general the aim is to secure a well-crystallised compound which has a definite melting point.

APPENDIX I

Pressure of Aqueous Vapour.

<i>Temp. °C.</i>	<i>mm. Mercury</i>	<i>Temp. °C.</i>	<i>mm. Mercury.</i>
0	4.6	11	9.8
1	4.9	12	10.5
2	5.3	13	11.2
3	5.7	14	12.0
4	6.1	15	12.8
5	6.5	16	13.6
6	7.0	17	14.5
7	7.5	18	15.5
8	8.0	19	16.5
9	8.6	20	17.5
10	9.2		

Acids.

Mineral acids are bought either as "Commercial" or "For Analysis." In making up solutions for standardisation the latter quality is desirable. For one litre of approximately Normal acid the following volumes of concentrated acid should be diluted to make one litre:

	<i>Sp. gr. at 15° of conc. acid.</i>	<i>Per cent. solution.</i>	<i>Volume for 1 litre of N. acid.</i>
H ₂ SO ₄	1.84	96	28 c.c.
HCl	1.16	31.5	100 c.c.
HNO ₃	1.41	68.0	65 c.c.

Indicators.

The following are the pH ranges and colour changes of some common indicators.

	<i>pH range.</i>	<i>Colour change.</i>
Thymol Blue	1.2- 2.8	red-yellow
Methyl Orange	3.0- 5.0	orange-red-yellow
Methyl Red	4.4- 6.0	red-yellow
Litmus	6.0- 8.0	red-blue
Phenolphthalein	8.3-10.0	none-red
Thymolphthalein	10.0-11.0	none-blue
Resorcin Yellow	11.0-12.0	green-yellow-orange.

Absolute Alcohol.

This is a very expensive substance, and it must not be used for any purpose for which industrial spirit or methylated spirit would be satisfactory. It is stored in a well-stoppered bottle which contains some quicklime or anhydrous copper sulphate.

Ordinary industrial spirit may be rendered suitable for most of the organic preparations described in this book by allowing it to stand for a few days over anhydrous copper sulphate. When dried in this way the alcohol should not cause a fresh specimen of anhydrous copper sulphate to turn blue.

Distillation* of industrial spirit yields a constant-boiling mixture with water (95.6 per cent. alcohol by weight). To free the alcohol from water it may be dehydrated by boiling gently with quicklime under a reflux condenser. About one-tenth of the weight of alcohol is a suitable weight of freshly ignited quicklime to use. Alternatively, magnesium turnings or ribbon may be used, with a trace of solid mercuric chloride. The flask is heated on the water bath for at least four hours. The alcohol is then distilled on the water bath after a further quantity of quicklime has been added. The boiling point of the anhydrous alcohol is 78.4° C. at 76 cm. mercury pressure.

For larger quantities of absolute alcohol a different method may be employed. This consists in distilling a mixture of alcohol and one-quarter of its volume of benzene. A mixture of all three components—alcohol, water and benzene—comes over first, then benzene and alcohol distil and finally pure alcohol alone. This has the disadvantage of being somewhat expensive as a laboratory method.

The Cleaning of Apparatus.

All apparatus used in analysis or in the preparation of inorganic compounds must be washed thoroughly with water immediately after use. It should then be wiped dry with a clean cloth or allowed to drain in a rack.

Apparatus which has been used for the preparation of organic compounds is frequently contaminated with tarry or carbonaceous material which is not removed by water or dilute acid or alkali. A little methylated spirit or acetone solvent should be tried in the case of a tar. After draining out, the vessel is rinsed with water and then a little concentrated nitric acid may be cautiously introduced. If heat is applied it must be done very carefully since a vigorous action may develop, accompanied by sudden evolution of brown fumes. In the more stubborn cases potassium chromate solution, to which has been added half its volume of concentrated sulphuric acid, may be used. The apparatus should be left to stand with this solution in it overnight. In all cases, when the deposit has been removed, the apparatus should be well washed with water.

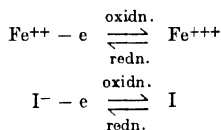
The Drying of Apparatus.

When a piece of apparatus is required to be clean and dry, all water should be drained out and then it is rinsed with a little methyl alcohol or acetone. While blowing air from a bellows into the apparatus by means of a glass tube reaching as far as possible, the apparatus is rotated slowly. If it is made of thin glass it may be held in the hot air above a wire gauze heated by a Bunsen burner—not over the flame itself. Thick glass apparatus is never heated.

* *Note.* Such distillation without permission by the Commissioners of Customs and Excise is illegal in England.

APPENDIX II

To compare oxidising or reducing agents systematically it is necessary to introduce the idea of the oxidation-reduction potential. The full theoretical treatment of the subject cannot be given here. As has been mentioned, however, an oxidation-reduction change concerning electrolytes can be represented as a transfer of electrons:



A platinum electrode, dipping into a solution containing the oxidising agent and its reduction product, will develop a charge, the sign and magnitude of which depend on the position of equilibrium. An oxidising agent will tend to remove electrons from the platinum and thus render it positively charged. The magnitude of the charge may then be used to place the oxidising agent with respect to other agents. To standardise the conditions the oxidising agent and its reduced form are present in molar concentration, and the platinum electrode is coupled with a Normal hydrogen electrode so that the E.M.F. of the cell can be found. The following results, which have been published, illustrate the matter.

<i>Oxidising agent.</i>	<i>Change involved.</i>		<i>Potential</i>
KMnO ₄	MnO ₄ ⁻ + 8H ⁺ + 5e	⇌ Mn ⁺⁺ + 4H ₂ O	+ 1.52 volts.
KBrO ₃	BrO ₃ ⁻ + 6H ⁺ + 6e	⇌ Br ⁻ + 3H ₂ O	+ 1.48
Ce(SO ₄) ₂	Ce ⁺⁺⁺⁺ + e	⇌ Ce ⁺⁺⁺	+ 1.45
K ₂ Cr ₂ O ₇	Cr ₂ O ₇ ⁻ + 14H ⁺ + 6e	⇌ 2Cr ⁺⁺⁺ + 7H ₂ O	+ 1.3
O ₂	$\frac{1}{2}$ O ₂ + 2H ⁺ + 2e	⇌ H ₂ O	+ 1.23
FeCl ₃	Fe ⁺⁺⁺ + e	⇌ Fe ⁺⁺	+ 0.75
I ₂ (in KI)	$\frac{1}{2}$ I ₂ + e	⇌ I ⁻	+ 0.54
<i>Reducing agent.</i>			
SnCl ₂	Sn ⁺⁺	⇌ Sn ⁺⁺⁺⁺ + 2e	- 0.14
CrCl ₂	Cr ⁺⁺	⇌ Cr ⁺⁺⁺ + e	- 0.40
Zn	Zn	⇌ Zn ⁺⁺ + 2e	- 0.76

The potentials given are based on the arbitrary supposition that the Normal hydrogen electrode develops zero potential. Unfortunately the table cannot be applied in any very simple manner, since the potentials are found to be affected by the presence of other ions and also must be corrected for the actual concentrations present. Thus ferrous sulphate has a higher potential in dilute sulphuric acid than it has in water, and this agrees with the well-known fact that the substance is more quickly oxidised by air when in neutral solution. But these effects are themselves useful. The presence of phosphoric acid is found to lower the potential

of ferric chloride, and this is the reason for using phosphoric acid in conjunction with diphenylamine indicator (p. 76).

***A Short Table of Atomic Weights (1940 values)**

Aluminium	Al	26.97	Lead	Pb	207.21
Antimony	Sb	121.76	Lithium	Li	6.94
Arsenic	As	74.91	Magnesium	Mg	24.32
Barium	Ba	137.36	Manganese	Mn	54.94
Bismuth	Bi	209.00	Mercury	Hg	200.61
Boron	B	10.82	Nickel	Ni	58.69
Bromine	Br	79.92*	Nitrogen	N	14.01*
Cadmium	Cd	112.41	Oxygen	O	16.00
Calcium	Ca	40.08	Phosphorus	P	30.98
Carbon	C	12.01	Platinum	Pt	195.23
Cerium	Ce	140.13	Potassium	K	39.096
Chlorine	Cl	35.46*	Silicon	Si	28.06
Chromium	Cr	52.01	Silver	Ag	107.88
Cobalt	Co	58.94	Sodium	Na	23.00*
Copper	Cu	63.57	Strontium	Sr	87.63
Fluorine	F	19.00	Sulphur	S	32.06
Gold	Au	197.20	Tin	Sn	118.70
Hydrogen	H	1.008	Titanium	Ti	47.90
Iodine	I	126.92	Vanadium	V	50.95
Iron	Fe	55.85	Zinc	Zn	65.38

* These values have been given correct to two places of decimals although the 1940 table gives them to three places.

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	16	20	24	28	32	37
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	28
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13	15	18	20	23
18	2558	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	6	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	6	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	7	9	10	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4773	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	8	9
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	6	7	8	9
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	6	7	8	9
49	6902	6911	6920	6929	6937	6946	6955	6964	6972	6981	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	4	5	6	7	8	9

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LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	4	5	6	7	8	9
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	3	4	5	6	7	8	9
53	7243	7251	7259	7267	7276	7284	7292	7300	7308	7316	1	2	3	4	5	6	7	8	9
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	3	4	5	6	7	8	9
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	3	4	5	6	7	8	9
57	7559	7568	7574	7582	7589	7597	7604	7612	7619	7627	1	2	3	4	5	6	7	8	9
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	2	3	4	5	6	7	8	9
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	2	3	4	5	6	7	8	9
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	2	3	4	5	6	7	8	9
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	2	3	4	5	6	7	8	9
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	2	3	4	5	6	7	8	9
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	2	3	4	5	6	7	8	9
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	2	3	4	5	6	7	8	9
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	2	3	4	5	6	7	8	9
66	8195	8202	8209	8216	8222	8228	8235	8241	8248	8254	1	2	3	4	5	6	7	8	9
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	2	3	4	5	6	7	8	9
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	2	3	4	5	6	7	8	9
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	2	3	4	5	6	7	8	9
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	2	3	4	5	6	7	8	9
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	2	3	4	5	6	7	8	9
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	2	3	4	5	6	7	8	9
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	2	3	4	5	6	7	8	9
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	2	3	4	5	6	7	8	9
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	2	3	4	5	6	7	8	9
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	2	3	4	5	6	7	8	9
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	2	3	4	5	6	7	8	9
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	2	3	4	5	6	7	8	9
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	2	3	4	5	6	7	8	9
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	2	3	4	5	6	7	8	9
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	2	3	4	5	6	7	8	9
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	2	3	4	5	6	7	8	9
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	2	3	4	5	6	7	8	9
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	2	3	4	5	6	7	8	9
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	2	3	4	5	6	7	8	9
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	2	3	4	5	6	7	8	9
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	2	3	4	5	6	7	8
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	2	3	4	5	6	7	8
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	2	3	4	5	6	7	8
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	2	3	4	5	6	7	8
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	2	3	4	5	6	7	8
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	2	3	4	5	6	7	8
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	2	3	4	5	6	7	8
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	2	3	4	5	6	7	8
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	2	3	4	5	6	7	8
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	2	3	4	5	6	7	8
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	2	3	4	5	6	7	8
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	2	3	4	5	6	7	8
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	2	3	4	5	6	7	8

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